Ion Beam Formation and Modification of Metallic Nanoparticles

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A thesis submitted for the degree of Doctor of Philosophy of the Australian National University
Declaration

Due diligence is the best of the author's knowledge and belief, no material
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This thesis contains, to the best of the author’s knowledge and belief, no material previously published by another person or submitted for a degree or diploma at any university except where due reference is made in the text.

B. Johannessen
To those I know will never really read this thesis.
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Abstract

This thesis investigates the growth and stabilization of carbonaceous nanoparticles formed in amorphous SiO$_2$ by the pyrolysis of an alkane precursor. It was suggested that pyrolyzing a precursor (alkane SiO$_2$) with the desired species (carbon) on the surface of the nanoparticles are commonly formed from annealing, while the carbon species have sufficient kinetic energy to diffuse within the matrix. These effects play a major role in the overall behavior and stability of the nanoparticles. Their overall structure and the incorporation of in novel device applications. This thesis studies the fundamental physical properties, namely, the short-range atomic structure, of carbonaceous nanoparticles. The short-range atomic structure consists of electron scattering rings, forming shells of an atom in the material. This structure is responsible for the observed electron absorption line structure (ESALIS) spectra, while electron microscopy techniques using high brilliance synchrotron arrays. Complementary information was obtained extensively utilizing transmission electron microscopy (TEM), x-ray diffraction (XRD), and wide angle x-ray scattering (WAXS). For example, WAXS was used to determine the nanoparticle morphology, XRD to determine the crystallographic phases and WAXS to infer the nanoparticle distribution.
Abstract

This thesis investigates the growth and modification of metallic nanoparticles formed in amorphous SiO$_2$ by ion implantation and thermal annealing. By supersaturating a matrix (here SiO$_2$) with the desired species (here Cu or Zn atoms) nanoparticles are commonly formed upon annealing when the implanted atoms have sufficient kinetic energy to diffuse within the matrix. Given finite-size effects for nanoparticle less than about 100 nm in diameter, where the under-coordinated surface atoms play a major role, their overall atomic structure is generally subtly different from that of their bulk counterparts. Such differences can be taken advantage of in novel device applications. This thesis studies the fundamental physical properties, namely the short-range atomic structure, of embedded nanoparticles. The short-range atomic structure consists of the few nearest neighboring shells of an atom in the material. The structure is elucidated by extended x-ray absorption fine structure (EXAFS) spectroscopy measurements performed using high-brilliance synchrotron x-rays. Complementary techniques were also employed extensively, including transmission electron microscopy (TEM), x-ray diffraction (XRD) and small angle x-ray scattering (SAXS). For example, TEM was used for observing the nanoparticle morphology, XRD to determine the crystallographic phase and SAXS to extract the nanoparticle size distribution.

Two formation studies were undertaken. One investigated the ion beam syn-
thesis of Cu nanoparticles and the other of Zn nanoparticles. In its bulk form Cu is a face-centred cubic (fcc) material, while Zn is hexagonally close-packed (hcp). For the former the first nearest neighbor shell, containing 12 atoms in its bulk form, was analyzed. For the hcp structure, on the other hand, the first nearest neighbor is split in two shells. Each contains 6 atoms in its bulk form, that are only separated by ~ 0.3 Å (in the case for Zn). Both these shells were analyzed together.

For the Cu study it was found that spherical nanoparticles formed readily upon annealing, exhibiting the fcc structure. The short-range atomic structure of the nanoparticles varied as a function of size. For example, the bond length contracted with decreasing nanoparticle diameter. Measurements of the bond length contraction were used to establish the surface tension of the nanoparticles, which was found to correspond to several GPa of pressure exerted on the nanoparticle core. This is greater than that of free-standing nanoparticles and hence exemplifies the influence the embedding matrix has on the nanoparticles. Similarly, the structural disorder (measured in terms of the Debye-Waller factor by EXAFS) increased with decreasing nanoparticle size. The relationship between size and Debye-Waller factor indicated that the disorder was predominantly located at the nanoparticle surface, consistent with its reconstruction.

For the Zn study it was verified that spherical nanoparticles formed upon annealing at high temperatures only and then exhibited the hcp structure. The short-range atomic structure of these nanoparticles was, however, difficult to elucidate stemming from parameter correlations.

The last study investigated ion irradiation of Cu nanoparticles. This was undertaken in order to increase the structural disorder of the nanoparticles and create an amorphous metallic phase. Such effect has not been achieved by ion
irradiation of bulk elemental metals, given the high regeneration rate. However, in this thesis, strong evidence is presented for the amorphization of metallic nanoparticles. This process is explained in terms of finite-size effects. The amorphous structure consisted of an average bond length expansion, increased Debye-Waller factor and a bond length distribution skewed towards longer bond lengths. The pre-irradiation structure was recovered upon low temperature annealing. These results represent the first report on the amorphization of elemental metallic nanoparticles by ion irradiation.
Publications

Journal publications


- R. Johannesson, P. Kloth, N. Ghilian, L.L. Aranjo, D.J. Jessefert, C.J.
Publications

Journal publications


- B. Johannessen, P. Kluth, R. Giulian, L.L. Araujo, D.J. Llewellyn, G.J.


Refereed conference publications


Other publications


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Chapter 1

Introduction and Background

This chapter opens with a general introduction and brief thesis outline. This is followed by sections 1.2 and 1.3, which provide an introduction particular to metallic nanoparticles and outline a range of production techniques. The nanoparticle production technique of choice for this thesis, ion beam synthesis, is outlined in further detail in section 1.4. Section 1.5 discusses nanoparticle properties with an emphasis on atomic structure deviations as compared with the bulk. Further motivations to the research presented in this thesis are given in section 1.6, which includes a theoretical discussion of ion-irradiation-induced amorphization.
Nanoscience and technology are research sectors on which much effort is now focussed. Today there are special purpose funding programs in place in major parts of the industrialized world, including the National Nanotechnology Initiative in the USA [1], the Nanotechnology Action Plan for the EU [2] and the Australian Research Council Nanotechnology Network in Australia [3]. Nanoscience and technology has also entered into popular science via television, radio, newspapers and the internet. The science which governs materials on this length scale is truly fascinating. Whereas both atomic physics and condensed matter physics are well understood, the processes which occur in the transition between the two is less well understood, and thus forms the basis for the research reported in this thesis.

Small clusters of atoms form a state of matter that can neither be described as a bulk solid nor as an ensemble of single atoms. These clusters, or nanoparticles, of characteristic length 1 to 100 nm, have physical and chemical properties that differ significantly from those of their respective bulk counterparts. Such differences arise from two factors. As the size of a macroscopic particle is reduced, the number of atoms at the surface of the particle compared to the total number of atoms in the particle increases. For example, a 100 nm diameter Cu nanoparticle, containing several million atoms, has a surface-to-bulk ratio (SBR) of about 1% meaning that about 1% of the atoms are located at the surface. In comparison, a 10 nm nanoparticle contains several thousand atoms and has a SBR of about 10%, while a 2 nm nanoparticle contains several hundred atoms and has a SBR of about 45%, etc. Figure 1.1 shows the estimated SBR and total number of atoms in face-centred cubic (fcc) Cu nanoparticles as a function of diameter. As the nanoparticles get smaller, properties which are usually determined by the atomic structure of the bulk lattice become increasingly dominated by the structure at
1.1. INTRODUCTION TO THE NANOWORLD

Figure 1.1: Estimated surface-to-bulk ratio and total number of atoms for Cu nanoparticles of face-centred cubic structure of given diameter. The estimate used a lattice constant of 0.361 nm.
Figure 1.2: Density of states in bulk metal and metal nanoparticles.

The second phenomenon, also related to the finite nanoparticle size, is referred to as quantum confinement. It arises because the size of the nanoparticle is comparable to the de Broglie wavelength of the charge carriers (electrons). In other words, the electrons are confined spatially and the occupied and unoccupied bands split into discrete electronic levels, as shown graphically in Figure 1.2 for a metallic nanoparticle as compared with its bulk counterpart.

1.1.1 A brief outline of this thesis

This thesis discusses the ion beam synthesis of embedded metal nanoparticles (Cu and Zn) and their short-range atomic structure. The latter is measured by extended x-ray absorption fine structure (EXAFS) spectroscopy. EXAFS is a powerful technique, which can elucidate deviations in the bond length distribution of atoms in nanoparticles as compared to their bulk counterpart. Given the finite-size and increased structural disorder in nanoparticles, ion irradiation is applied to
enhance the disorder and potentially create an amorphous metallic phase (Cu). This is not achievable for the bulk mono-metallic structure due to the rapid regeneration of the face-centered cubic (fcc) lattice.

The thesis consists of eight chapters as follows:

**Chapter 1:** the remainder of the current chapter provides the background and motivation to the research presented in this thesis.

**Chapter 2:** outlines the basic theory behind the EXAFS technique, which is the single most significant experimental technique utilized here.

**Chapter 3:** provides a background to all the experimental techniques utilized, including sample preparation for synchrotron x-ray experiments.

**Chapter 4:** gives a detailed description of EXAFS data analysis procedures used in this thesis.

**Chapter 5:** discusses ion beam synthesized Cu nanoparticles.

**Chapter 6:** considers ion beam synthesized Zn nanoparticles.

**Chapter 7:** examines ion irradiation of Cu nanoparticles.

**Chapter 8:** contains conclusions and suggestions for future research.

### 1.2 Historical recap: Metallic nanoparticles

Historical findings suggest that metallic nanoparticles were first produced in lustred pottery in Iraq, in the early ninth century AD, using a combination of glazing and kiln techniques [4]. Lustred pottery is characterised by striking metallic reflections and iridescence originating from the presence of metallic nanoparticles.
as discovered about 1000 years later [5]. Figure 1.3 shows examples of lustred pottery from Renaissance Italy, where the red and golden colors have recently been attributed to the presence of Cu and Ag nanoparticles, respectively [5].

In more recent times, Faraday was an early pioneer in nanoparticle research when preparing Au nanoparticles from the reduction of a Au salt liquid solution [7]. His publication from 1857 describes the characteristic ruby color of the reduced solution and postulates that this color is due to the small particle size. Indeed, Au nanoparticles interact strongly with visible light at around 520 nm. At this wavelength the free electrons of the nanoparticles collectively oscillate as schematically presented in Figure 1.4 and the radiation is preferentially absorbed. This phenomenon is known as the surface plasmon resonance (SPR) [8]. About 50 years later, in 1908, Mie presented the mathematical framework [9] which related the size of the nanoparticle to the position of the SPR absorption peak. Smaller nanoparticles would experience a blue shift (< 520 nm), while larger nanoparticles would experience a red-shift (> 520 nm). As the emission wavelengths of nanoparticles depend on their size, they can be used to tune the wavelength of “quantum dot” lasers [8].
1.3 Production techniques

There is a wide variety of techniques for producing nanoparticles. Some common ones include: condensation from a vapor, chemical synthesis, ultrasonic synthesis, mechanical processes such as milling and implantation techniques. A brief description of each technique follows.

1.3.1 Vapor condensation

Conceptually, this technique involves evaporation of a solid metal followed by rapid condensation to form metallic nanoparticles that settle in the form of a powder [10]. Inert gases are used when producing metallic nanoparticles (an oxidizing agent can be used if desired). Particle size is controlled by variation of the synthesis parameters such as the temperature and evaporation rate.

1.3.2 Chemical synthesis

The widely used chemical synthesis technique is essentially based on growing nanoparticles from a liquid medium consisting of various reactants. For example,
Au nanoparticles can be produced in water by the reduction of HAuCl$_4$ in a boiling sodium citrate (Na$_3$C$_6$H$_5$O$_7$) solution [11]. The nanoparticle size can be tuned by varying the concentration ratio between the Au salt and the sodium citrate [11].

### 1.3.3 Ultrasonic synthesis

Ultrasonic treatment initiates acoustic cavitation in a chemical solution, which can collapse into nanoparticles of the desired species. For example, Cu nanoparticles can be produced by exposing a wet copper hydrazine carboxylate (CHC) complex to high-power high-intensity (100 W/cm$^2$) ultrasound radiation [12]. The CHC solution is kept under Ar gas throughout the radiation to prevent oxidation. The resulting metallic lustred slurry, consisting of Cu nanoparticles in solution, is then centrifuged, washed and dried [12]. Nanoparticle size control can be achieved through adding additional solvents or changing the radiation parameters.

### 1.3.4 Ball milling

High energy ball milling is a “top-down” approach for nanoparticle production. Macroscopic starting point materials (powders) are placed in a mill where they collide with macroscopic high speed ceramic balls. This induces defect production including dislocations and new grain boundaries, which results in a polycrystalline powder with a minimum grain size of, for example, about 20 nm for fcc Zn and Cu [13]. Particle size can be influenced by the kinetic energy of the ceramic balls and the milling time.
1.3.5 Ion implantation

Ion implantation is an established technique commonly used in the semiconductor industry. It is very versatile and can be used to incorporate nearly any ionic species into a wide range of hosts. It is a highly non-equilibrium process not limited by solubility issues. By implanting a certain concentration of impurities and subsequently performing a thermal treatment at elevated temperatures, nanoparticles may form. It is possible to accurately control the number of implanted ions (which strongly affects the final nanoparticle size) and the nanoparticle formation process is thus highly reproducible. It is the technique of choice for this thesis, and a more thorough explanation follows below. Additionally, Chapter 3 outlines the technical aspects of operating the ion implanter.

1.4 Ion beam synthesis: Formation and growth

During ion implantation, each ion penetrates the surface of the target and loses energy via electronic and nuclear stopping processes. Electronic stopping is the slowing down by means of interactions between the electrons bound to target atoms and the incoming ion [14]. This is an inelastic process and can lead to the excitation of both target atoms and the incoming ion. Nuclear stopping are elastic collisions between the incoming ion and the nuclei of target atoms [14]. This usually causes the formation of defects in the target, including point defects such as vacancies and interstitials [15].

Figure 1.5 shows the basic steps in forming nanoparticles by ion implantation. In (a) each incoming ion interacts stochastically with the target atoms and comes to rest after a sequence of energy loss processes as explained above. In (b), after implanting a high fluence (ions/cm$^2$) of the same ionic species at the
same energy, a depth distribution of implanted ions is formed. In the absence of diffusion, the depth distribution can be roughly approximated by a Gaussian function centered at a projected depth range [16]. The depth distribution is a function of the ion species and energy and of the nature of the target. As nuclear stopping is dominant at low energies, target defects will always be a part of the ion implantation process. This is shown in Figure 1.6, where the calculated vacancy and Cu concentration is plotted as a function of target depth for 2.3 MeV Cu ions implanted into SiO₂. The target structure can be restored by thermal annealing, which also enables the implanted atoms to diffuse. This can lead to the formation of nanoparticles [17], particularly if the atomic concentration of impurity atoms is above the solubility limit, as illustrated in Figure 1.5(c).

This last step, precipitation of nanoparticles, is rather complex and not fully understood. Issues such as the implanted ion diffusivity and solubility in the host (target) and chemical interaction between the implanted ion and host atoms can strongly influence the nanoparticle formation process [17]. For example, the implantation of a SiO₂ target involves the production of point defects including dangling Si and O bonds [18]. Implantation of an ion that is strongly electronegative, such as F [19], can result in F-Si bonds, while the implantation of an atom with lesser electronegativity, such as Cu [19], can result in Cu-O bonds [18]. Ignoring such issues, which depend on the specific ion/target nature, it is commonly agreed that the precipitation of nanoparticles (Figure 1.5(c)) can be divided into three steps, which are not strictly separated [17]. They are: (1) nucleation, (2) diffusion-limited growth and (3) Ostwald ripening. Implantation-induced defects may act as nucleating centers initiating the formation of nanoparticles. During thermal annealing the nanoparticles grow by depleting their immediate surroundings of implanted atoms. This process is diffusion-limited in that the extent of
1.4. ION BEAM SYNTHESIS: FORMATION AND GROWTH

Figure 1.5: Cartoon of ion beam synthesis of nanoparticles in a substrate. (a) Each implanted ion interacts stochastically with the target losing energy until it comes to rest. (b) After implanting to high fluence a depth distribution of implanted atoms is formed. (c) By heating the sample, the atoms acquire sufficient kinetic energy to form nanoparticles, which can grow further by Ostwald ripening as explained in the text.
1.0 - • V • Cu atoms 
• Vacancies • • •

Figure 1.6: TRIM simulations for 2.3 MeV Cu ions implanted into a SiO$_2$ target [16]. The target vacancy and Cu concentration is plotted as a function of target depth.
the “immediate surroundings” is determined by the annealing temperature, annealing time and diffusivity of the implanted species [17]. This can be understood as non-competitive growth, in that each nanoparticle grows at the expense of dissolved implanted atoms, without interacting directly with each other. For longer annealing times the last stage, Ostwald ripening, becomes important. Ostwald ripening is a competitive growth process [20] where larger nanoparticles grow at the expense of smaller ones, whereby the total surface energy is reduced. In general, as a result of the nucleation and growth process described above, the final depth distribution of nanoparticles is similar to the depth distribution of implanted ions.

1.5 Metallic nanoparticle properties

As a consequence of their finite-size, nanoparticle properties often differ from those of their bulk counterparts, including structural, electrical, magnetic, optical and chemical properties [21]. As the present thesis will focus on the atomic structure of metallic nanoparticles, the following section will outline the relevant issues regarding this topic.

1.5.1 Atomic structure

As discussed above, with a decrease in size the fraction of surface atoms increases significantly for clusters with diameters less than 100 nm. In terms of short-range atomic structure, it is also obvious that the average coordination number will decrease given the fraction of under-coordinated surface atoms. Simplistically, this means that, while a fcc nanoparticle has a first nearest neighbor coordination number of 12 atoms in the bulk volume (internal), an atom located at the sur-
Figure 1.7: Average coordination number in the first nearest neighbor shell as a function of nanoparticle diameter.

Surface will have a coordination number that is approximately halved. Figure 1.7 shows the calculated coordination number of the first nearest neighbor for Cu nanoparticles as a function of diameter, assuming the fcc structure and considering the influence of the SBR only [22]. Clearly, the average coordination number is expected to be much reduced for small nanoparticles.

Simulations of metallic nanoparticles applying well-tested many-body potentials confirm the simple picture described above [23]. Figure 1.8(a) shows that for a Au nanoparticle containing 887 atoms the coordination number at the surface is about half that of the internal atoms. Comparable results were found for other metals including Cu [23]. Concurrently, as shown in Figure 1.8(b), a bond
1.5. METALLIC NANOPARTICLE PROPERTIES

Figure 1.8: Calculated (a) coordination number $N$ and (b) bond length $R_b$ for a Au nanoparticle [23]. Each column represents a “shell” of atoms (one bond length). The atoms at the surface (the outer shell) have a much reduced $N$ and $R_b$, while deep inside the nanoparticle each atom has the bulk values for $N$ and $R_b$. Horizontal, vertical and net lines represents the surface shell, transition shell and the core region, respectively, as defined by the authors in [23].

Length contraction was found for atoms located within the surface region. Bond length contraction in metallic nanoparticles is well known and can be understood in terms of a surface tension $\gamma$ arising from the nanoparticle surface curvature. A simple liquid-drop model relates the bond length contraction, $\delta R$, with $\gamma$ [24]:

$$\delta R = \frac{4}{3} \cdot (1/D) \cdot KR_b\gamma \quad (1.1)$$

where $K$ is the bulk compressibility, $R_b$ is the bulk bond length and $D$ is the nanoparticle diameter.

Thus the bond length contraction increases with decreasing nanoparticle size.
This picture is, however, not unmitigated. Although most metals show a bond length contraction, certain metals do not. This includes Zn, Cd and Hg in group IIB, which have been reported with an outward surface relaxation [26]. A chemical explanation proposes that these elements do not bind strongly when they have few neighbors due to energy gain arguments [26]. For example, the Zn dimer has a bond length that is 50% greater than the bulk value [27].

We have seen that for nanoparticles, given the increased SBR, the coordination number and bond length are different from those of their bulk counterparts. At the surface the atoms do not occupy ideal lattice position and, due to their reduced coordination number, the Coulomb interactions with their neighbors are different from atoms in the bulk of the nanoparticles [28]. The perturbed Coulomb interactions give rise to increased structural disorder including an anharmonic bond length distribution. Failure to take this anharmonicity into account may cause errors in the evaluation of the structural parameters of the nanoparticles [29].

### 1.5.2 Vibrational properties

When an atomic lattice is heated, heat transfer occurs through the individual vibrations of atoms about their equilibrium positions, until all lattice atoms are set in motion [30]. The vibrational density of states (VDOS) can be determined as a function of the phonon frequency $\nu$ (the quantized mode of vibration), as shown in Figure 1.9 [31]. Here the simulated VDOS for a generic fcc material is plotted as a function of $\nu$ at several temperatures. The bottom and top graphs are the solid before melting and after recrystallization, respectively. The overlapping peak profile is characteristic for fcc materials [31]. Note that these simulations are performed within a zero pressure environment.
Figure 1.9: Evolution of the VDOS for a generic fcc material at zero pressure. In (a) the solid is at the melting temperature, in (b) superheated, in (c) molten, in (d) supercooled and in (e) the supercooled liquid has recrystallized [31]. The plots have been offset.
Figure 1.10(a) shows the simulated VDOS for an individual Cu nanoparticle (consisting of 791 atoms) as a function of $\nu$ and compared with that of bulk fcc Cu [32]. Qualitatively, the two profiles are comparable, although for the nanoparticles the tails at both low and high $\nu$ are greater than for the bulk fcc Cu. In order to understand this difference, the VDOS for the nanoparticle can be separated into surface and bulk contributions as shown in Figure 1.10(b). The surface tension, discussed above, imposes a capillary pressure on the nanoparticle core, thus shifting this contribution to the VDOS towards greater $\nu$, which is equivalent to "stiffer" bonds [32]. Meanwhile, the disordered and under-coordinated surface results in "looser" surface bonds, which shifts the VDOS towards smaller $\nu$. When the nanoparticle size decreases both the capillary pressure and SBR increase. The net effect is therefore the result of two competing contributions [33]. This causes, to a certain extent, smearing of the VDOS.

Finally, Figure 1.11 shows the simulated VDOS for bulk fcc Cu compared with a polycrystal (consisting of 8.2 Å grains) and the amorphous structure [33]. The polycrystalline sample exhibits an extended VDOS towards both low and high $\nu$, which is in qualitative agreement with the simulations presented in Figure 1.10(a) for an individual nanoparticle. The amorphous VDOS is comparable to that of the polycrystalline sample, though a much more smoothly varying function.

1.5.3 Interaction with a matrix

Thus far the discussion has focussed on free-standing metallic nanoparticles not confined by a host matrix. However, the interaction between the nanoparticles and a matrix may influence the nanoparticle characteristics. Brief examples of this are provided in the following paragraphs.

Given differences in thermal expansion between the nanoparticles and the ma-
Figure 1.10: Simulated vibrational density of states (VDOS) [32]. In (a) the VDOS for bulk fcc Cu and a Cu nanoparticle (791 atoms) is shown, while in (b) the surface and core contributions for the latter are shown.
Figure 1.11: Simulated vibrational density of states (VDOS) for bulk fcc Cu, polycrystalline Cu and amorphous Cu (glass) [33].
trix, for specific annealing temperatures the matrix may exert pressure on the nanoparticles, increasing the structural disorder of the latter [34]. Also, while the ion implantation into an amorphous matrix generally results in spherical nanoparticles, a crystalline matrix may favor the formation of faceted nanoparticles [35]. Obviously, this can influence the atomic structure and result in phase changes dependent on nanoparticle size or formation parameters [35].

While the nanoparticle shape may depend on the nature of the matrix, superheating of nanoparticles has been reported for both crystalline [35] and amorphous [36] matrices. In the latter report, it was suggested that interfacial energies (between the matrix and the liquid/solid nanoparticles), as opposed to epitaxy, are influencing the melting point characteristics of embedded nanoparticles. Recently, non-linear optical properties of Cu nanoparticles embedded in crystalline and amorphous SiO$_2$ were investigated [37]. The third order susceptibility, indicative of nanoparticle formation, was dependent on the implantation flux (current density), but not on the nature of the matrix.

In the present thesis, Cu and Zn nanoparticles were synthesized by ion implantation into amorphous SiO$_2$, the latter grown by wet thermal oxidation of Si(100). SiO$_2$ is an excellent electric insulator and is compatible with current all-optical integrated circuit technology [38]. Also, the thermal expansion coefficient of the Si substrate is greater than that of the SiO$_2$ [19]. This makes the latter compressively strained after annealing, thus more resistant to cracking, and the Si can act as a heat sink in potential high-power applications [39].
1.6 Motivation for this study

Rao and Cheetham state in their recent Feature Article *Science and technology of nanomaterials: current status and future prospects* that [40]:

> there will be progress in the discovery and commercialization of nanotechnologies and devices ... bound to have an impact on the chemical, energy, electronics and space industries ... Our capability to synthesize, organize and tailor-make materials at the nanoscale is, however, of very recent origin ... immediate goals ... to fully master the synthesis of isolated nanostructures ... with the desired properties ... to generate new classes of high performance materials.

This thesis is intended as a contribution towards a fuller understanding of the synthesis mechanism and properties of embedded metallic nanoparticles. These materials are receiving attention due their potential applications in, for example, non-volatile memories [41], optical filters [42] and thermal and optical switching devices [43, 44].

Additionally, this thesis is motivated by the possibility of creating an *amorphous* elemental metallic structure through the ion irradiation of metallic nanoparticles. This has not been achieved previously and could have applications in, for example, optical devices due to modification of the optical properties [45].

1.6.1 Ion-irradiation-induced amorphization

Ion irradiation has long been used as a tool for producing disordered or amorphous semiconductors, the latter being an atomic structure lacking long-range order beyond a few neighboring shells. Within the semiconductor industry, ion irradiation of both elemental and alloyed semiconductors are commercially pur-
sued to introduce impurities and/or defects that are beneficial both for electronic and optoelectronic devices [45].

Conversely, while both alloyed and elemental semiconductors can be amorphized by ion irradiation, the bulk elemental metallic structure cannot be rendered amorphous by self-implantation where the original structure retains chemical purity [46]. Amorphous metals have only been achieved by implanting chemical impurities, for example Al irradiated with Ni [47] or Ni irradiated with P [46]. Typically the impurity concentration is in the order of 10 - 20 at.% for the amorphous phase to stabilize.

Theoretical studies of ion implantation of elemental semiconductors and metals in their bulk form show that point defects, such as interstitials and vacancies, are produced in both the open diamond structure (semiconductors) and the close packed metallic structure [48]. However, the latter exhibits strong damage regeneration leading to much smaller amounts of final damage, as shown in Figure 1.12. Ion implantation causes collision cascades of displaced atoms that exhibit a liquid like character with a lifetime of $\sim 10^{-12}$s [49]. The extent of such regions are shown in Figure 1.12(a). This liquid-like region consists of a highly disordered atomic structure [50], which can potentially be quenched in to form an amorphous phase. However, the dissipation time of residual kinetic energy (the time required for the cascade to cool down) is not fast enough to quench in the amorphous state in the close packed metallic structure [48]. For semiconductors, the open nature of the diamond structure and the slow regeneration of damage due to covalent bonding enhance residual damage [48]. The result of this is shown in Figure 1.12(b). The amount of disorder in elemental metals thus saturates prior to the formation of an amorphous phase [48].

Recently, experimental studies of ion irradiation of semiconductor nanoparti-
Figure 1.12: Simulations of 10 keV self-cascades in Ge and Au. In (a) the maximum number of "liquid" atoms in the collision cascades are highlighted, while (b) shows the residual defects after the cascades have cooled down [48].
icles, such as Si [51] and Ge [52], showed that the nanoparticles were rendered amorphous at fluences below that required for the bulk counterpart. For example, Figure 1.13 shows the Debye-Waller factor\(^1\) of the first nearest neighbor shell in Ge (bulk and nanoparticles) as a function of irradiation fluence [52]. The saturation of the Debye-Waller factor was consistent with the lack of long-range order (beyond the first nearest neighbor) and the formation of an amorphous phase. It was reported that the nanoparticles were rendered amorphous at nearly two orders of magnitude less fluence than the bulk. Several potential causes for the rapid amorphization of the nanoparticles were suggested [52], all originating from finite-size effects. For example, the greater pre-irradiation Debye-Waller factor of the nanoparticles is equivalent to a higher-energy structural state and related to the increased SBR and disordered surface atoms. Considering the irradiation yields an increase in free energy per atom, the higher-energy state of the nanoparticles prior to irradiation potentially reduces the fluence required for amorphization [52]. Similarly, in bulk semiconductors it has been reported that the surface is rendered amorphous well before the rest of the crystal given the disorder that is also present at the surface of bulk materials [51]. Recent experimental results [53] suggest that the surface reconstruction of embedded Ge nanoparticles occurs through the formation of amorphous-like layers, as predicted by simulations [54]. This strengthens the rationale given above.

The intriguing question we seek to answer in this thesis is thus whether it is possible to reach the elemental metallic amorphous phase via ion irradiation of elemental metallic nanoparticles.

\(^1\)The Debye-Waller factor was measured through the use of x-ray absorption spectroscopy as discussed in Chapter 2.
Figure 1.13: Debye-Waller factor (measured by x-ray absorption spectroscopy) as a function of Si irradiation fluence comparing the polycrystalline (bulk) and nanocrystalline (nanoparticles) Ge samples [52].
1.7 Summary

This chapter has given a general introduction and motivation to the research presented in this thesis. In summary, we have seen that the finite size of nanoparticles has a significant influence on the short-range atomic structure. For example, the under-coordinated surface atoms are reconstructed such that the overall structural disorder is greater in small nanoparticles as compared with the bulk. This thesis investigates the formation of metallic nanoparticles in SiO₂ by ion implantation and then the use of high-energy ion irradiation to induce further disorder and amorphization.

The following chapter gives a theoretical background to the extended x-ray absorption fine structure technique, which was employed to measure the short-range atomic structure of the nanoparticles.
Chapter 2

EXAFS Theory

This chapter describes the theoretical aspects of the extended x-ray absorption fine structure (EXAFS) technique. Section 2.1 outlines the general approach to EXAFS, followed by an overview of the theoretical concepts and mathematical formulations used in EXAFS analysis. This chapter also discusses the practical aspects of data collection and analysis, including sample preparation, data reduction, and interpretation of the results.
Chapter 2

EXAFS Theory

This chapter describes the theoretical aspects of the extended x-ray absorption fine structure (EXAFS) technique. Section 2.1 explains the general information present in an x-ray absorption spectrum, while section 2.2 concentrates on the modulated extended x-ray absorption region.

The absorption edge is characterized by a steep increase in the absorbance of the material and corresponds to the binding energies of electrons in the K or L shell of the absorbing atom. Figure 2.1 shows the absorption as a function of energy through the K-edge of polycrystalline Cu. In this region, electrons from the valence band to the conduction band are excited into the continuum. The former provides insight into the chemistry of the absorbing atom, i.e., the ionic state. For instance, an edge shifted noticeably at higher energy can arise from an electron in a higher oxidation state, as observed for Cu+ ions in Chapter 6. This observation is explained by the core electron being more tightly bound to the nucleus as a result of reduced screening from the lesser number of valence electrons.
2.1 X-ray absorption

X-ray absorption was first explained a century ago in terms of the photoelectric effect [55] in which a high-energy photon is absorbed by matter and its energy transferred to a bound electron, which may then be able to overcome the binding energy and escape its atom of origin. The Beer-Lambert law for the absorption of monochromatic x-rays in matter states that the measured transmitted intensity $I$ is given by an exponential attenuation law [56]:

$$I = I_0 e^{-\mu x}$$

(2.1)

where $I_0$ is the initial intensity, $x$ is the sample thickness, and $\mu$ is the linear x-ray absorption coefficient. In general the latter decreases with photon energy except when the energy is comparable to that of an occupied electronic state, known as the absorption edge.

The absorption edge is characterized by a sharp increase in the absorbance of the material and corresponds to the binding energies of electrons in the K, L, M, etc, orbitals of the absorbing atom. Figure 2.1 shows the absorbance as a function of energy through the K-edge of polycrystalline Cu. As indicated, there are two regions of interest. The x-ray absorption near edge structure (XANES) includes core electrons (here K orbital) being excited into an outer bound orbital, while the extended x-ray absorption fine structure (EXAFS) reflects core electrons being excited into the continuum. The former provides insight into the chemistry of the absorbing atom, e.g. the oxidation state. For example, an edge shifted towards a higher energy can arise from an atom in a higher oxidation state, as observed for CuO (see e.g. Chapter 6). This observation is explained by the core electrons being more tightly bound to the nucleus as a result of reduced screening from the lesser number of valence electrons.
2.1. X-RAY ABSORPTION

Figure 2.1: X-ray absorption spectrum for a Cu reference foil at the K-edge, measured in transmission mode at 12 K.

2.1.1 EXAFS region

Analysis of the EXAFS region, starting $\sim 30$ eV beyond the edge [57], is the primary technique for the work presented in this thesis. An isolated atom would display an absorption dependence ($\mu_0$) approximately proportional to $E^{-3}$:

$$\mu_0 \approx \frac{\rho Z^4}{AE^3}$$  \hspace{1cm} (2.2)

where $\rho$ is the sample density, $Z$ is the atomic number, and $A$ is the atomic mass. It is clear that the above energy dependence does not hold for an atom that forms part of a network, e.g. metallic Cu as presented in Figure 2.1. We will now explore the impact of the atomic neighborhood and discuss the equation governing the extended x-ray absorption region.
2.2 Fundamentals of EXAFS

Consider an atom absorbing a photon of sufficient energy to excite a core shell electron. The kinetic energy of the excited photoelectron is given by the difference between the photon energy and the binding energy of the electron. When the kinetic energy is sufficient for the photoelectron to be excited into the continuum, it may interact with the surrounding neighborhood (atoms). Treating the photoelectron quantum mechanically as an outgoing spherical wave, its wavelength $\lambda$ is given by:

$$\lambda = \frac{h}{p}$$  \hspace{1cm} (2.3)

where $h$ is Plank's constant and $p$ is the momentum of the photoelectron, which (in the EXAFS region) is given by:

$$\frac{p^2}{2m} = h\nu - E_0$$  \hspace{1cm} (2.4)

where $m$ is the electron mass, $\nu$ is the photon frequency and $E_0$ is the binding energy of the electron.

The ejected photoelectron wave can scatter from atoms in close proximity to the absorbing atom. The scattered wave will thus interfere with the outgoing wave as schematically represented by Figure 2.2. The superposition of the waves determine the final state of the absorber and the backscattering event(s) will thus modify the probability of x-ray absorption [57]. The modulations in the EXAFS region as seen in Figure 2.1 are a direct consequence of the wave nature of the photoelectron. The peaks and valleys correspond to the outgoing and scattered waves being in phase or out of phase, respectively. The phase difference depends on the distance between the absorbing and backscattering atoms as well as the photoelectron wavelength, while the oscillation amplitudes depends on the backscattering strength (function of the atomic number) for each scatterer.
With a more quantitative description of EXAFS it is thus possible to extract information of the local atomic environment surrounding the absorbing atom.

### 2.2.1 The EXAFS equation

The standard equation for EXAFS oscillations, $\chi(k)$, due to single scattering events by $j$ atoms surrounding an absorber is given by \[57\]:

$$
\chi(k) = \frac{\mu - \mu_0}{\mu_0} = 3 \sum_j \frac{m}{2\pi\hbar^2 (kr_j)^2} \cos^2 \theta_j \sin[2kr_j + \delta_j(k)]
$$

(2.5)

where the photon energy $E$ is substituted with the wavenumber $k$ as given by the following relation:

$$
k = \frac{\sqrt{2m(E - E_0)}}{\hbar}
$$

(2.6)

and where $r_j$ is the position of the $j$th atom, $f_j(k)$ is the backward scattering amplitude function, $\theta_j$ is the angle between the polarization direction of the absorbed photon and the bond direction of the scatterer and $\delta_j(k)$ is the phase shift due to the position of the central atom. Further details and derivation of Equation 2.5 can be found elsewhere \[57\].
The following discussions will justify subtle additions and modifications to the EXAFS equation as given above. It will incorporate the physical platform needed for the extraction of the atomic structure of the materials investigated in the present work.

**Lifetime**

The excitation of a photoelectron is synonymous with the production of a core hole. In Equation 2.5 the lifetime of both the photoelectron and the core hole has been neglected. The former will lose energy via inelastic scattering, while the latter will decay by e.g. Auger transitions. Both effects are of comparable magnitude and can be included in the EXAFS theory via a mean free path $\lambda(k)$, which is the distance the photoelectron travels in a given time without inelastic scattering or filling of the core hole (typically $\lambda \approx 8\dd{Å}$). The probability of this occurring is given by $\exp(-2r_j/\lambda)$ and thus Equation 2.5 becomes [57]:

$$\chi(k) = 3 \sum_j \frac{m}{2\pi\hbar^2} f_j(k) \exp\left(-\frac{2r_j}{\lambda(k)}\right) \frac{\cos^2 \theta_j \sin[2kr_j + \delta_j(k)]}{(kr_j)^2}$$  \hspace{1cm} (2.7)

**Gaussian disorder**

Thus far the expression for EXAFS assumes the summation of neighboring atoms located at well defined distances $r_j$ from the central absorber (the location of the scattering atom being mathematically defined as a $\delta$-function). In an EXAFS experiment typically $10^{10}$ absorptions take place, and EXAFS is thus a superposition of all such absorber / scatterer environments. Noting that the scattering process lasts in the order of $10^{-16}$ s, while the period of thermal vibrations is $\sim 10^{-13}$ s, the measured EXAFS will be a superposition of environments with a distance distribution in $r_j$ due to disorder. The concept of a shell structure is introduced, where each shell consists of chemically identical scatterers located at
a common \( r_j \) (e.g. for crystalline Cu the first nearest neighbor shell contains 12 Cu scatterers located at \( \sim 2.5 \text{ Å} \) from the central absorber). Including *minimal* static disorder (e.g. for crystalline samples), the distribution of bond lengths is given by a Gaussian distribution \( \exp(-2k^2\sigma_{\text{total}}^2) \) where \( \sigma_{\text{total}}^2 \) is the Debye-Waller factor:

\[
\sigma_{\text{total}}^2 = \sigma_{\text{thermal}}^2 + \sigma_{\text{static}}^2
\]  

(2.8)

The modified EXAFS equation is then [57]:

\[
\chi(k) = 3 \sum_j \frac{m}{2\pi\hbar^2} f_j(k) \exp\left(-\frac{2r_j}{\lambda(k)} - 2k^2\sigma_{\text{total}}^2\right) \frac{\cos^2 \theta_j \sin[2kr_j + \delta_j(k)]}{(kr_j)^2} \]  

(2.9)

As noted above, this is valid for a Gaussian distribution of interatomic distances only. A more general approach needs to include non-Gaussian disorder, applicable for nanoparticles as studied in the present work, taking into consideration higher order cumulants of the distribution, as presented in section 2.2.2.

**Angular dependence**

For a randomly oriented sample, such as a polycrystalline or nanocrystalline sample, Equation 2.9 must be averaged over the angle between the bond direction and the photon polarization direction, \( \theta_j \). A space random average yields \( \langle \cos^2 \theta_j \rangle = 1 \) and thus the equation for \( \chi(k) \) becomes [57]:

\[
\chi(k) = \sum_j \frac{m}{2\pi\hbar^2} f_j(k) \exp\left(-\frac{2r_j}{\lambda(k)} - 2k^2\sigma_{\text{total}}^2\right) \sin[2kr_j + \delta_j(k)]
\]  

(2.10)

**Multielectron effects**

The description of EXAFS has assumed that the ejection of a photoelectron excited the atom into a well defined state, ignoring the other electrons in the system. However, multielectron excitations may occur in which the energy absorbed from the photon is shared by more than one electron. In the creation
of a core hole, additional loosely bound electrons may be affected by the lesser screening of the positively charged nucleus and Coulomb interactions with the emitted photoelectron [57]. The extra electron may be excited to outer bound states ("shake-up") or into the continuum ("shake-off"). Multielectron effects are approximately constant as a function of $k$ [58]. The result of this is a smearing of the EXAFS oscillations, which can be accounted for by a $S_0^2$ amplitude reduction factor (i.e. $S_0^2 \leq 1$). The amplitude reduction factor is dependent on the absorbing atom, but less so on the chemical state of the absorber. For example the $S_0^2$ of metallic and oxidized Cu are comparable [57]. With the choice of a suitable reference compound (e.g. polycrystalline Cu for the Cu nanoparticle study) the amplitude reduction factor can be determined by the reference and kept at constant value during the analysis of the nanoparticle samples.

The EXAFS equation for single scattering in a randomly oriented system with Gaussian disorder and containing $N_j$ atoms in a shell at a distance $r_j$, including multielectron effects can now be written:

$$
\chi(k) = \sum_j \frac{N_j}{kr_j^2} S_0^2 F_j(k) \exp\left(-2r_j/\lambda(k) - 2k^2\sigma_{total}^2\right) \sin[2kr_j + \delta_j(k)]
$$

(2.11)

where $F_j(k) = \frac{m}{2\pi\hbar^2k} f_j(k)$ is the effective amplitude function.

**Multiple scattering**

The development of the EXAFS equation given by Equation 2.11 above assumes interference between the outgoing wave and the wave scattered of one neighboring atom [57]. *Multiple* scattering occurs when the electron wave has scattered off two or more neighbors. The effective scattering path is determined by the geometry of the scatterers and will necessarily be larger for a multiple scattering path as compared to single scattering with an atom in the nearest neighbor shell. For example, in crystalline Cu the first nearest neighbor shell is located at $\sim 2.5$ Å.
from the central absorber, while the first multiple scattering path has an effective distance of \( \sim 3.8 \, \text{Å} \). In the present work only the first nearest neighbor shell was analyzed, for which multiple scattering paths are negligible [59].

2.2.2 Cumulant expansion

The cumulant expansion [57] is suitable for describing systems with moderate non-Gaussian disorder. In the Gaussian disorder limit, the model will be equivalent to the harmonic approximation presented in section 2.2.1. Below follows a brief description of the derivation of the cumulant-expanded EXAFS equation.

For an anharmonic system the disorder term present in Equation 2.11 is no longer valid. A more exact approach is to show that the EXAFS Debye-Waller factor term is in general complex and has a natural cumulant expansion in powers of \( k \) (MacLaurin series expansion about \( k = 0 \), while assuming \( \delta \) to be independent of \( k \)) i.e. [60]:

\[
\langle \exp(i2k(\vec{r} - \bar{r})) \rangle = \exp \sum_{n=0}^{\infty} \frac{(i2k)^n}{n!} C_n = \exp(-W + i\phi)
\]  

(2.12)

where \( \bar{r} \) is the mean position, \( C_n \) is the \( n \)th-order cumulant average of the distance distribution and \( W \) and \( \phi \) are the real and imaginary parts of the exponent, respectively. Expanding the sum of Equation 2.12 gives:

\[
C_0 + i2kC_1 - 2k^2C_2 - i\frac{4}{3}k^3C_3 + \frac{2}{3}k^4C_4 + \ldots
\]  

(2.13)

and thus the real part depends only on even powers of \( k \), while the imaginary part depends only on odd powers of \( k \).

Choosing \( \bar{r} \) as the centroid of the distribution and normalizing the latter gives \( C_1 = 0 \) and \( C_0 = 0 \), respectively, and thus [57]:

\[-W = -2k^2C_2 + \frac{2}{3}k^4C_4 + \ldots\]

(2.14)
and

\[ i\phi = -i\frac{4}{3}k^3C_3 + \ldots \] (2.15)

where the real part gives the following contribution to the EXAFS equation:

\[ \exp(-2k^2C_2 + \frac{2}{3}k^4C_4 + \ldots) \] (2.16)

while the imaginary part gives a contribution of:

\[ \sin(-\frac{4}{3}k^3C_3 + \ldots) \] (2.17)

The cumulant-expanded EXAFS equation is thus written as follows:

\[
\chi(k) = S_o^2 \frac{F(k)}{kC_1^2} N \exp(-2C_1/\lambda) \exp(-2k^2C_2 + \frac{2}{3}k^4C_4 + \ldots) \sin(2kC_1 - \frac{4}{3}k^3C_3 + \ldots + \Phi(k))
\] (2.18)

where \( \Phi(k) \) is the total phase shift (corresponding to the influence of the change in peak position of the distance distribution [57]), \( N \) is the total number of atoms in the given shell and \( F(k) \) is the amplitude function of the atoms in the given shell. The four leading cumulants are expressed relative to \( \bar{r} \) [61]:

\[
C_1 = \langle (r - \bar{r}) \rangle
\] (2.19)

\[
C_2 = \langle (r - \bar{r})^2 \rangle \equiv \sigma_{total}^2
\] (2.20)

\[
C_3 = \langle (r - \bar{r})^3 \rangle
\] (2.21)

\[
C_4 = \langle (r - \bar{r})^4 \rangle - 3\sigma_{total}^4
\] (2.22)

EXAFS analysis, as presented in Chapter 4, can be employed to extract the cumulants for each atomic shell about the absorbing atom. Typically, for nanoparticle systems, inclusion of the first three cumulants was essential to accurately determine the atomic radial distribution function.
2.2.3 Theoretical standards (FEFF)

For the work presented in this thesis both the bulk crystalline and nanoparticle samples were fitted to a theoretical standard (FEFF [62]). The atomic structure of particular interest (i.e. that for the nanoparticle samples) is thus directly comparable to that for their bulk counterparts. The FEFF code calculates \textit{ab initio} values for the absorbing and scattering atoms including phase shifts, effective scattering amplitudes and scattering paths (single and multiple) in clusters of atoms greater than the mean free path of the photoelectron [59, 63].

2.3 Summary

In summary, the theoretical background to the EXAFS study presented in this thesis has been given. We have seen that EXAFS is sensitive to the superposition of all local atomic environments probing the region within one mean free path from the absorber.

The following chapter gives a mainly technical background to \textit{all} the experimental techniques utilized in the present work.
Chapter 3

Experimental Techniques
Chapter 3

Experimental Techniques

This chapter describes theoretical and technical aspects of the experimental techniques used in this thesis. There are two main groups of techniques, those used for the formation (sections 3.1 and 3.2) and those used for the characterization of nanoparticle samples (sections 3.3-3.6).
3.1 Ion implantation

Ion implantation is a materials engineering process commonly used in semiconductor device fabrication by which energetic ions are implanted into a target material. The ions may introduce both chemical and structural changes to the target, in that they are commonly a different element than the target and that the target can be damaged by the energy loss process of the incident ion, respectively (see Chapter 1).

The present work uses primarily a National Electrostatics Corporation (NEC) 5SDH-4 tandem accelerator (1.7 MV) as presented schematically in Figure 3.1. Both lower energy (175 kV accelerating voltage) and higher energy (14 MV accelerating voltage) accelerators were used for some part of the work, but will not be discussed here as their principles of operation are in effect the same.

The NEC ion implanter uses a SNICS-type (Source of Negative Ions by Cesium Sputtering) source as presented schematically in Figure 3.2. The atomic species to be implanted is commonly packed as a solid or powder into a Cu cathode. The cathode is then inserted into the SNICS source where a pressure of $10^{-6}$ Torr is achieved prior to operation. Cs vapor comes from the Cs oven and into the enclosed area between the cooled cathode and the heated ionizing surface ($\sim 1100^\circ$C). Some of the Cs condenses on the front of the cathode whilst some is ionized by the hot ionizer surface. Positively charged Cs ions accelerate towards the cathode through a potential difference and sputtering occurs from the cathode through the condensed Cs layer. Sputtered particles will gain electrons as they pass through the condensed Cs layer, producing a negatively charged beam. The ion beam is accelerated away from the cathode and through the aperture in the ionizer to the positively biased extractor end of the source ($\sim 15$ kV).

An additional acceleration section, know as the source bias (\(~ 65$ kV) and
3.1. ION IMPLANTATION

Figure 3.1: Schematic diagram of a 1.7 MV tandem accelerator (NEC, 5SDH-4) located at the Department of Electronic Materials Engineering at the Australian National University.
an Einzel lens are used to increase the particle energy and focus the beam, respectively. This enables improved species resolution in the mass analyzing 90° magnet. By setting the magnetic field ($B$) such that the magnetic force acting on the accelerated ions is equal to the centripetal force of the ions as they are deflected through a radius ($R$), the required ions with mass ($m$) and charge ($n$) will be deflected towards the low energy end of the accelerator tank, i.e.:

$$B = \frac{1}{R} \sqrt{\frac{2mV_i}{qn}}$$ \hspace{1cm} (3.1)

where $V_i$ is the potential of the ions and $q$ is the electronic charge.

The beam is delivered by the magnet to another Einzel lens and electrostatic steerers for injection into the accelerator tank. The high voltage terminal (1.7 MV maximum) resides in the middle of the tank containing pressurized SF$_6$ gas for insulation purposes. Positive charge is supplied to the terminal by two pelletron chains. The beam of negative ions is accelerated to the positively charged terminal where they are partially stripped of electrons by N$_2$ charge exchange. The positive beam is then accelerated to the downstream end of the tank where the final energy of the ions, $E_f$, is:

$$E_f = q[V_i + (1 + n)V_i]$$ \hspace{1cm} (3.2)

Figure 3.2: Schematic diagram of a typical SNICS source.
where $V_t$ is the voltage at the terminal and $V_i$ is potential at the injector end of the accelerating tank.

A $15^\circ$ energy analyzing magnet is used to select ions of the desired species and charge state (i.e. $q = +1, +2, +3$, etc.) following the same principle as for the $90^\circ$ magnet (see Equation 3.1). A quadrupole lens is employed to bring a suitably focussed ion beam onto the target in the implant chamber. The beam is scanned across the target in $x, y$ direction (raster scanned) until the required implant fluence ($Q$) is achieved. The latter can be expressed as an integral over time ($t$):

$$Q = \frac{1}{qAn} \int_0^t idt$$  \hspace{1cm} (3.3)$$

where $i$ is the beam current and $A$ is the implanted area (determined by a tantalum metal aperture at the entrance to the target chamber). Samples discussed in the present work were most commonly thin film SiO$_2$-on-Si, which was held onto a Ni sample holder by steel clips and/or conductive C paste for optimum thermal contact. The pressure in the target chamber was typically $10^{-7}$ Torr to minimise contamination. Secondary electrons were suppressed by a Cu cage maintained at -300 V surrounding the target. The Cu cage was also cooled by liquid N$_2$ to condense any residual contaminant molecules in the chamber.

### 3.1.1 Simulation software

Ion implantation ranges and energy losses due to electronic and nuclear processes were calculated using the TRIM (Transport of Ions in Matter) code [16], a Monte Carlo computer simulation program capable of performing detailed numerical calculations for individual ion-substrate interactions. For detailed intermixing studies (ion irradiations in Chapter 7) a modified TRIM code (TRIDYN [64]), taking dynamic composition changes into account, was used. TRIDYN incorpo-
rates compositional changes both due to the spatial redistribution of target atoms in the collision cascades and due to the presence of the implanted ions.

3.2 Thermal treatment

Thermal treatment (up to 1100 °C) was performed in a conventional horizontal single-zone quartz tube furnace (Lindberg) in a flowing forming gas ambient (5% H₂ in N₂). Samples were resting on a pristine SiO₂-on-Si wafer in a silica glass boat, to minimize the chance of contamination, which was placed in the tube furnace following stabilization of the operating temperature.

3.3 Rutherford backscattering spectrometry

Rutherford backscattering spectrometry (RBS) is a well established technique for performing quantitative materials analysis [65]. RBS is based on the collision between atomic nuclei and involves measuring the number and energy of ions in a mono-energetic (MeV) beam, which backscatter after colliding with atoms in the near-surface region of a sample at which the beam has been targeted. Figure 3.3 shows a schematic diagram of the principle of RBS. Though the majority of the incident particles are simply implanted into the target material, a small fraction undergo a direct Coulombic collision with a nucleus in the target. This collision can be accurately modeled as an elastic collision using classical physics, while assuming the absence of nuclear reactions and resonances [65]. The energy of the backscattered ions are measured by a surface barrier detector fixed at a scattering angle of 168°. The particle energy measured by the detector is dependent on the incident particle energy, penetration depth, stopping cross-section of the target material (both before and after the scattering event) and the scattering event.
The latter is commonly referred to in terms of the kinematic factor \((K)\):

\[
K = \frac{E_s}{E_i} = \left[ \frac{1 - \left( \frac{M_1 \sin \theta}{M_2} \right)^2}{1 + \frac{M_1 \cos \theta}{M_2}} \right]^{1/2}
\]

where \(E_s\) and \(E_i\) are the energies immediately before and immediately after the scattering event, respectively, \(M_2\) and \(M_1\) are the masses of the incident ion and target atom, respectively, while \(\theta\) is the scattering angle. Thus, knowing the incident ion beam properties (species, charge state and energy) the energy measured for each backscattered ion quantitatively reflects target atomic composition and depth profile thereof.

The RBS measurements presented in this work were performed using a NEC 5SDH tandem accelerator (1.7 MV). The design of the RBS equipment is similar to that of the ion implanter (section 3.1), however it uses a different ion source and the high-voltage tank has only one pelletron chain. The latter is sufficient for RBS measurements, which typically require a nA beam (for ion implantation a \(\mu\)A beam is commonly desired). The biased ion source uses a RF (radio frequency) field to positively ionize a (typically) He gas that is bled into the source area. On leaving the source, the ions pass through a charge exchange chamber.
containing Rb vapour, which negatively charges the ions. This type of RBS source is thus commonly referred to as a Rb (Rubidium) source. Detailed description of equipment and operations can be found elsewhere [66].

### 3.4 X-ray diffraction

X-ray diffraction (XRD) is a well known and widely used technique for phase identification in both bulk crystalline samples and nanoparticle samples. For the latter, nanoparticle size, strain and disorder in addition to instrumental specifics may limit its application [67]. XRD uses x-rays emitted from a conventional source or a synchrotron source (see section 3.6), which are aimed at the target material. For the work presented in this thesis a Philips Analytical XRA400 diffractometer was employed with a conventional Co x-ray tube (\( K_\alpha = 1.789 \, \text{Å} \)) operated at 40 kV and 30 mA to investigate implanted thin film SiO\(_2\) samples.

When an x-ray is scattered off an atom in the target, it will interfere as any electromagnetic wave with x-rays scattered off other target atoms. For a target with a crystalline or partially crystalline lattice nature (such as nanoparticles) the interference is constructive, leading to pronounced peaks in the XRD pattern, when Bragg’s condition is satisfied [67]:

\[
    n\lambda = 2d \sin \theta \tag{3.5}
\]

where \( n \) is an integer, \( \lambda \) is the wavelength of the x-rays, \( d \) is the interplanar spacing and \( 2\theta \) is the scattering angle. Thus, the crystallographic structure of the sample can be determined through the measuring of the intensity of the scattered x-rays as a function of \( 2\theta \).
3.5 Transmission electron microscopy

It is well known that the maximum resolution of a microscope is limited by the wavelength of the photons used to probe the sample. Visible light has wavelengths of 400–700 nm and can be used with relative ease in a conventional visible light microscope. However, further improvement in resolution necessitates ultraviolet light, for which sample absorption becomes a problem, or x-rays, for which the lack of interaction with the sample is limiting its applicability. A solution to this problem is the exploitation of the wave nature of electrons as first postulated by de Broglie in 1925 [68]. The wavelength (\(\lambda\)) of an electron is related to its accelerating energy \(V\):

\[
\lambda = \frac{h}{\sqrt{2meV}}
\]  

(3.6)

where \(h\) is Planck's constant, \(m\) and \(e\) are the electron mass and charge, respectively. Electrons can thus be accelerated to high energies to achieve short wavelengths, thus improving the resolution of the microscope [68].

Transmission electron microscopy (TEM) is a powerful tool for materials characterization [68]. For the work presented in this thesis, TEM provided information about nanoparticle shape, size and phase. Figure 3.4 shows a schematic diagram of a typical electron microscopy setup. A cathode and acceleration stage ensure the production of a monochromatic electron beam, which, much like in an optical microscope, is focussed onto the sample by lenses. It interacts with the thin sample by elastic and inelastic scattering, as shown in Figure 3.5. By placing an aperture to only allow the direct beam through, a bright field image is created. Depending on the composition of the sample (for example nanoparticles in \(\text{SiO}_2\)) and their respective interaction with the incoming electron beam a contrasted image is created. This image can be projected onto a fluorescent screen,
Figure 3.4: Schematic diagram of a transmission electron microscope. The magnetic lenses, consisting of coils of wire carrying currents, are shown in cross section.
3.5. TRANSMISSION ELECTRON MICROSCOPY

Figure 3.5: Signals generated when a high-energy beam of electrons interacts with a thin specimen [68].

A photographic film or the screen of a digital camera.

The diffracted electron beams form an interference pattern, which can be used to identify the diffracting material (e.g. an ensemble of nanoparticles embedded in an amorphous matrix such as SiO₂), much the same way as that of x-ray diffraction. Figure 3.6 shows a comparison between x-ray and electron diffraction for an Al foil. For this thesis electron diffraction was used to complement XRD experiments. Electron diffraction patterns can be used to determine the interplanar spacing \( d \), given by [68]:

\[
Rd = \lambda L
\]

(3.7)

where \( R \) is the distance from the incident beam to the diffraction ring (as measured from the lower half image in Figure 3.6), \( \lambda \) is the wavelength of the electrons (as determined from a relativistic version of Equation 3.6), and \( L \) is the camera length. The latter is effectively the magnification value for the diffraction pattern. The electron diffraction patterns thus give information on the crystallographic structure or phase of the sample.
CHAPTER 3. EXPERIMENTAL TECHNIQUES

Figure 3.6: X-ray and electron diffraction. The upper half shows the diffraction of x-rays through an Al foil, while the lower half shows that for the diffraction of electrons.

3.5.1 Microscopy sample preparation

The main limiting factor in the use of an electron microscope is the mean free path of the electrons in the sample, which is inversely proportional to the energy. Electron microscopy thus desires high electron voltage and thin samples. Typically, thicknesses of the order of 100 nm are required.

For the present thesis, microscopy (Phillips CM300 operating with 300 kV electrons) was utilized to measure phase, size and size distribution of nanoparticles formed in amorphous thin film SiO\textsubscript{2}-on-Si by ion implantation. The SiO\textsubscript{2} thickness was 0.6 – 5.0 \(\mu\text{m}\) while that of the crystalline Si support was about 500 \(\mu\text{m}\). There are in general two ways of preparing a TEM sample, either for plan view or for cross sectional microscopy, as illustrated in Figure 3.7. The ion implantation profile is depth dependent, which typically results in the nanoparticle size distribution being depth dependent. The cross sectional TEM technique is thus favored to a plan view sample as the latter yields inferior depth resolution.

Figure 3.8 shows a step-by-step schematic for the preparation of cross sectional
TEM samples. Step A involves cutting and cleaning of a SiO$_2$-on-Si sample, typically to a 3x5 mm dimension. In step B, two such samples are glued face-to-face using an epoxy cured on a hotplate at $\sim 100^\circ$C. Two samples were used for either a greater success rate (if same samples) or greater efficiency (if different samples), while an additional stack of dummy wafers is attached for support. Note that the “success” of a TEM sample often cannot be determined until it has been observed in the microscope. The stack was then cut with a diamond wheel saw to few mm thickness (step C), and a 3 mm diameter disc was ultrasonically cored and centred about the interface to be examined (step D). In step E the core is mechanically ground to $\sim 100 \ \mu$m after which it is dimpled a further 80 - 90 $\mu$m. Finally, in step F, the dimpled region is ion milled until perforation, resulting in a thin edge ($\leq 100 \ \text{nm}$) in the area of interest (implanted SiO$_2$). For samples that are temperature critical (such as ion irradiated Cu nanoparticle samples, see Chapter 7) a variation to the procedure described above was implemented [69]. First, the sample was glued with an epoxy cured at room temperature while exposed to UV light and mechanical pressure. This necessitated the sample (SiO$_2$-on-Si) to be glued to a transparent glass slide, or within two glass slides (SiO$_2$.
Figure 3.8: Schematic of the sample preparation procedure for cross sectional transmission electron microscopy (not to scale). The final product requires dimensions not greater than 3 mm diameter and 100 μm outer rim thickness containing a thin edge (≤100 nm) in the area of interest. Details of steps A through F are explained in the text.
film without substrate). Mechanical grinding, dimpling and ion milling was in general performed as described above, however the ion miller stage was in thermal contact with a liquid $N_2$ reservoir to better suppress beam heating.

### 3.6 Synchrotron radiation techniques

Synchrotron radiation is the electromagnetic radiation generated by the acceleration of relativistic particles (commonly electrons or positrons) through magnetic fields. Synchrotron radiation was named after its discovery in a General Electric synchrotron accelerator built in 1946 [70]. Figure 3.9 shows a spot of light emerging from the transparent vacuum tube of the 70 MeV synchrotron built in the research laboratory of the General Electric Company in Schenectady, New York. This was the first visual observation of such radiation, which had been predicted nearly four decades earlier [71].

![Figure 3.9: The 70 MeV General Electric synchrotron with clearly visible synchrotron radiation spot (red arrow) radiating from the transparent vacuum tube (first observations 1947).](image)

Synchrotron radiation has a range of unique properties, including:

**high brightness** many orders of magnitude greater than conventional x-ray
tubes

**high collimation** the photon beam has a small angular divergence

**low emittance** the product of source cross section and solid angle of emission is low

**wide energy spectrum** with tunable energy output by monochromatization

**polarized** a high level of polarization, linear or elliptical

**pulsed light emission** pulse duration typically below one nanosecond

Such radiation has thus become a powerful tool in a range of research fields including physics. In particular, for the work presented in this thesis, hard x-rays (energies of several keV) were applied to investigate the atomic structure, size distribution and crystallographic structure of embedded metallic nanoparticles (sections 3.6.2 and 3.6.3). Such measurements require a careful sample preparation method, as presented in section 3.6.4.

### 3.6.1 Generation of synchrotron radiation

As mentioned above, a charged particle moving through a magnetic field will be affected by a Lorentz force and, as a result, diverge from a linear path. In the process the particle will loose energy in the form of electromagnetic radiation emitted tangential to the particle path. For particles with energy $E$, the energy of the emitted *photons* is [72]:

\[
E_p = \frac{hE^3}{2\pi rm^3c^5}
\]

where $h$ is Plank’s constant, $r$ is the radius of curvature, $m$ is the particle mass and $c$ is the speed of light. Note that the photon energy is proportional to the
cube of the particle energy, while inversely proportional to the radius of curvature. Thus, for photon energies ranging up to several keV and a fixed particle mass (positrons or electrons are used), it is necessary with a large particle energy. This in turn requires strong magnetic fields to sufficiently confine the particle beam in a closed loop structure. For example, the Advanced Photon Source (APS) at the Argonne National Laboratories (ANL, USA) operates with 7 GeV positrons and electromagnetic fields of 0.6 T [73]. Figure 3.10 shows a simplified schematic of a typical synchrotron (upper panel). The main components are as follows (a detailed description of the generation of synchrotron radiation is beyond the scope of this thesis. For more in-depth details, the reader is directed to [72]). Electrons are produced in an electron gun (A) then accelerated through a straight section (B) where, if required, a W film serves as a positron converter. Upon entering the booster ring (C), the particles will typically have an energy of a few hundred MeV [73]. In the booster ring they accumulate the operational maximum energy before being injected into the storage ring (D). The latter consists of a periodic magnet lattice, including magnets for bending and focusing (the latter not shown) of the particle beam, surrounding an ultra high vacuum particle chamber (\(\sim 10^{-10}\) Torr). Synchrotron radiation is emitted at bending magnets (as described above) and insertion devices (lower panel Figure 3.10, also known as wigglers or undulators). The insertion device uses a periodic array of alternating north-south electromagnets to "wiggle" the particle beam, thereby boosting both the photon brilliance and confinement [74]. Radio frequency cavities replenish the stored particle beam with energy lost by the generation of photons.

Each bending magnet and insertion device can accommodate several beamlines. The beamlines transport the photon beam to the experimental stations. Thus, each synchrotron facility operates a series of beamlines and experimental stations
Figure 3.10: Schematic of the basic principles of a synchrotron radiation facility. In the upper panel particles are produced at A, pre-accelerated at stages B and C and injected into the "storage ring" D. The main purpose of the latter is to produce synchrotron radiation while at the same time maintaining a constant particle energy. Synchrotron radiation is produced by magnets, for example a bending magnet or an insertion device (lower panel).
simultaneously and independently, for example the APS hosts about 40 beamlines and is one of the largest synchrotrons in the world.

The "raw" beam emitted via the storage ring magnets is polychromatic or "white", in that it contains a range of photon energies. Prior to entering the experimental station, a monochromatic, well focussed beam is required for the synchrotron radiation techniques applied in this thesis. Focussing is commonly handled by reflective mirrors and apertures. A set of crystals, which can typically both rotate and translate, diffract the beam according to Bragg’s law (Equation 3.5) to achieve a monochromatic beam.

3.6.2 EXAFS

A theoretical background to the extended x-ray absorption fine structure (EXAFS) is presented in Chapter 2. For a detailed outline of EXAFS data analysis the reader is referred to Chapter 4. Below we will concentrate on the experimental aspects of the EXAFS measurements performed for the work presented in this thesis.

Experimental modes

An EXAFS experiment measures the absorbance $\mu x$ as a function of the incident photon energy, starting just below an absorption edge and continuing to typically about 1 keV beyond the edge. There are two primary modes for data collection, transmission or fluorescence. The former measures $\mu x$ from the transmission of x-rays through the sample material as a function of the photon energy. Though a direct measure of the absorbance of the sample, it is a preferred method for homogeneous (and concentrated) samples only. The fluorescence mode measures the emission of fluorescent photons (one decay mechanism for the excited atom is
the filling of the core hole by an outer shell electron) as a function of the energy. Though an indirect measurement of the sample absorbance, it measures a signal proportional to $\mu x$ [75] and is well suited for inhomogeneous (and dilute) samples.

**Experimental setup**

EXAFS measurements were performed at the Australian National Beamline Facility (ANBF, beamline 20B) at the Photon Factory in Tsukuba, Japan, in collaboration with on-site scientist Dr. Garry J. Foran. Measurements were performed at the Cu and Zn K-edges (8.979 and 9.659 keV, respectively).

ANBF is a bending magnet beamline using a Si(111) double crystal monochromator. Figure 3.11 is a schematic of a typical setup for both fluorescence and transmission experiments. Due to the nature of the samples studied in this work (inhomogeneous and dilute) the former experimental mode was utilized, where the sample is rotated 45° with respect to the incident beam (for a transmission setup the sample is perpendicular to the beam). By orienting the solid state detector at 90° the solid angle seen by the detector is maximised. The monochromatic x-ray beam enters from the right through the first gas filled ionization chamber.

![Figure 3.11: Schematic (not to scale) of the experimental setup for EXAFS measurements at the ANBF beamline 20B (Photon Factory, Japan).](image-url)
(10, also known as the monitor) where the intensity is measured. The sample is mounted inside a He cryostat, which is typically kept at \(~12\text{K}\) to minimize thermally induced disorder. The fluorescent yield as a function of energy is measured by a multi-element Ge solid-state detector (the detector was upgraded from 10 to 36 elements in 2005). The first transmission chamber (11, also known as the detector) measures the intensity remaining after absorption by the sample. Following this is a homogeneous transmission reference foil and a third ionization chamber (12, also known as counter 3). The transmission setup can thus be used for energy calibration in a fluorescent experiment.

### 3.6.3 SAXS and WAXS

**Background**

The fundamental relation describing the scattering of x-rays by interaction with the electron densities in matter is given by Bragg’s law (Equation 3.5). It shows that the scattering angle varies inversely with the separation of the electron densities (equivalently lattice planes as measured by XRD). To study certain minerals and complex molecules with particularly large lattice spacings (in the order of tens or hundreds of interatomic distances) very small scattering angles, in the vicinity of the primary beam, need to be extracted [76]. Similarly, for the purpose of this thesis, x-ray scattering due to the presence of nanoparticles (i.e. electron densities) requires the extraction of scattered beams about 0.2 - 4 ° away from the primary beam. Using significantly longer wavelength photons, which in theory would result in the diffracted beams being further away from the primary, is in general not a feasible solution as they are strongly absorbed by matter.

Small angle x-ray scattering (SAXS) applied to the samples presented in

\[1\text{Assuming 1.54 Å x-rays and nanoparticles 1 - 20 nm in diameter.}\]
this thesis thus necessitated a highly collimated, high flux monochromatic beam achievable from a synchrotron source in combination with a high resolution detector system. A wide angle x-ray scattering (WAXS) setup, as shown below, can be interpreted the same way as a conventional XRD measurement.

Experimental details

SAXS and WAXS measurements were performed at the Consortium for Advanced Radiation Sources (Chemistry and Materials - ChemMatCARS, beamline 15ID-D) at the Advanced Photon Source in collaboration with on-site scientist Dr. David J. Cookson. SAXS measurements were performed with 1.06 - 1.5 Å photons (about 8.3 - 11.7 keV) to extract nanoparticle diameters of about 1 - 40 nm, while WAXS measurements were performed with 0.52 Å photons (about 24 keV) to extract lattice spacings of about 1 - 3 Å.

ChemMatCARS is an undulator beamline using a diamond(111) double crystal monochromator. Figure 3.12 is a schematic of the configuration for both SAXS and WAXS experiments. The monochromatic x-ray beam enters from the right.

Figure 3.12: Schematic (not to scale) of the experimental setup for SAXS / WAXS measurements at the ChemMatCARS beamline 15ID-D (Advanced Photon Source, USA).
The first PIN diode monitors the incident beam intensity prior to the sample, the latter positioned at normal incidence and at atmospheric pressure. Separating the vacuum and atmosphere are Kapton windows. Immediately after the sample is the camera vacuum tube, for which the length can be changed (about 6.8, 1.9 and 0.6 m cameras are available) to suit the particular experiment. For the SAXS measurements herein, the camera vacuum tube was either 1.9 or 0.6 m. The longest vacuum tube, at the energies listed in the previous paragraph, is suitable for very large particles greater than several hundred nm in diameter. The camera vacuum tube can be removed all together for a minimum sample-to-detector distance of about 100 mm suitable for WAXS experiments. At the camera entrance is a second PIN diode monitoring the transmitted beam intensity (the diode is fixed to a mechanical arm, which is moved out of the scattering path during measurements). Immediately prior to the exit of the camera is a direct beam stop (considering only a fraction of the beam is scattered, the direct beam will cause damage to the detector). After the Kapton window exit of the camera vacuum tube is a 6000 CCD detector, which measures the scattered intensity in the plane perpendicular to the primary beam. A scattering standard with a large well-defined d-spacing, such as silver behenate (AgC\text{22}H\text{43}O\text{2}, d-spacing 58.34 Å) is used for sample-to-detector distance calibration purposes.

**Data analysis**

The detector maps a two-dimensional scattering pattern, which is then integrated as a scattering intensity function dependent on the scattering angle, $2\theta(\degree)$, or equivalently the scattering vector, $Q(\text{Å}^{-1})$, from the primary to the scattered beam.

Figure 3.13 shows a representative WAXS pattern for crystalline Zn and Zn
Figure 3.13: WAXS spectra for crystalline hexagonal close packed Zn and Zn nanoparticles embedded in SiO₂. Some of the main diffraction peaks for crystalline Zn are indicated in the inset. Measurements were performed with 0.52 Å x-rays and a sample-to-detector distance of about 120 mm. On the right are the raw data from the detector. The primary beam is indicated by the circle (beam stop) at the end of the arm.

nanoparticles embedded in amorphous SiO₂. Such patterns can be interpreted the same way as XRD profiles are interpreted and thus gives information, in particular, about the crystallographic phase present. Figure 3.14 shows a representative SAXS pattern for embedded Cu nanoparticles. Scattering in the immediate vicinity of the beam stop or very far away from the beam stop is normally excluded due to detector overflow and background effects, respectively. Otherwise, scattering predominantly at low $Q$ is in general indicative of the presence of large nanoparticles (electron densities), while scattering predominantly at high $Q$ is
Figure 3.14: SAXS spectra for two SiO₂ embedded Cu nanoparticle samples measured using 1.5 Å x-rays and a sample-to-detector distance of about 1900 mm. The primary beam is indicated by the circle (beam stop) at the end of the arm (insets).
attributed to small nanoparticles (electron densities) following Bragg’s law of
diffraction (Equation 3.5).

The scattering intensity, $I(Q)$, can be expressed as an integral over the size
distributions of the nanoparticles, as given by [77]:

$$I(Q) = N_p \int_0^{\infty} p(R)|F(Q,R)|^2 dR$$  \hspace{1cm} (3.9)

where $N_p$ is the number of nanoparticles per unit sample volume, $p(R)$ is the
probability function of the nanoparticle size distribution, and $F(Q,R)$ is the form
factor of spherical nanoparticles with radius $R$ [77]. Thus, the SAXS profiles
may be used to quantitatively extract the corresponding size distributions. For
the present thesis, analysis to determine the size distributions were based on
an indirect transform method (ITM) or a maximum entropy method (MEM),
without using any presumed model for the distribution [77].

The ITM expresses the probability function, $p(R)$, as a linear expansion of a
set of cubic B-spline basis functions and uses Fourier transformations and least-
squares approximations to arrive at the most probable distribution function (for
further details see [78]). The MEM first expresses the nanoparticle size distri-
bution as a discrete probability distribution (with no unique solution) and then
selects a set of probability functions that maximizes the entropy of the system
thus arriving at the most probable size distribution (for further details see [79]).

The main differences between the two methods is that the MEM, unlike the ITM,
will never include physically impossible negative values in the size distribution,
while, on the other hand, the ITM has been found to perform better when limited
$Q$-range is available [77]. Both methods are implemented in the Irena SAS (small
angle scattering) software [80] which was used as a suite of the Igor Pro package
[81] for the purpose of analyzing SAXS data presented in this thesis.
3.6.4 Synchrotron sample preparation

To prepare the nanoparticle samples for synchrotron measurements it is advantageous to (1) remove the underlying substrate and (2) optimize the signal-to-noise ratio. Although SAXS/WAXS experiments are not count-rate limited the way (fluorescent) EXAFS is, it is important to eliminate parasitic scattering from the crystalline substrate by removal of the latter. For EXAFS measurements, the removal of the substrate enables optimization of the signal-to-noise ratio by stacking several SiO$_2$ films together. Figure 3.15 is a schematic outline for the synchrotron sample preparation procedure used in this thesis. Subsequent to nanoparticle formation the sample consisted of a thin SiO$_2$ film on a Si substrate (a). The former was about 0.6 - 5.0 $\mu$m thick, while the latter was about 500 $\mu$m. The substrate was mechanically ground to about 20 $\mu$m and the remainder was removed by a selective chemical etch (7g KOH:10mL H$_2$O) over about 15 hours (b). The substrate removal being complete, several SiO$_2$ films may be stacked together (c) for improved signal-to-noise and loaded into a 2x5 mm cavity in a multiple slot sample holder (d). The cavities were sealed with x-ray transparent Kapton films.

3.7 Summary

In summary, the experimental aspects and background to the sample preparation and characterization techniques utilized in this thesis: ion implantation, furnace annealing, RBS, XRD, TEM, EXAFS, SAXS and WAXS have been discussed.

The following chapter discusses general aspects of the extraction and analysis of EXAFS data.
Figure 3.15: Schematic (not to scale) showing the sample processing procedure for synchrotron experiments. In part (d) the right hand side is an image of the actual sample holder with outer dimensions 17x28 mm. Further details are given in the text.
Chapter 4

EXAFS Data Analysis

This chapter opens with a general introduction to EXAFS data analysis (section 4.1) and then describes the procedures used in this thesis. In sections 4.2 and 4.3 the extraction of the modulated region of an x-ray absorption spectrum is described, while in section 4.4 the procedure for analysis of the EXAFS data is described.

4.1 Introduction

Interpretation of EXAFS data is usually based on the EXAFS method, outlined in Chapter 3, including higher-order moments of the scattered electron

wave function and the techniques for fitting the various nonlinear effects. The method to which this is applied depends on the data set.

Various software packages have been developed to facilitate the analysis of EXAFS data, including EXCURV [72] and FEFFIT [35]. Both packages use

splitting of nearest-neighbor shells which, due to multiple-scattering, may be
impaired (particularly beyond the second or third nearest neighbors). The

FEFFIT approach takes advantage of Fourier Transform analysis of the EXAFS

spectra, the various shell contributions and its them individually to extract any
graphic structural parameters.

4.1.1 The FEFFIT software package

Figure 4.1 shows the structure of the FEFFIT software package. FEFFIT requires the algorithms of AUTOFIT [83] and FEFFIT [35]. The former removes the atomic background from a measured EXAFS spectrum, while the latter allows the experimental EXAFS to theoretical calculations from FEFF.
4.1 Introduction

Interpretation of EXAFS data is normally based on the EXAFS equation as outlined in Chapter 2, including higher-order cumulants of the radial distribution function (RDF) as necessary. The aim of the analysis is to determine structural parameters such as coordination number, distance and disorder of the atoms in the various coordination shells. The extent to which this is possible depends on the nature of the material and the quality of both standards and samples.

Various software packages have been developed to facilitate the analysis of EXAFS data, including GNXAS [82] and IFEFFIT [83]. Both incorporate a multiple-scattering approach. In essence, GNXAS fits the experimental raw data (without \textit{a priori} assuming separate nearest neighbor shells) to extract the RDF of the system. This procedure is particularly useful for highly disordered, non-static samples, such as liquids, for which there is a continuous distribution of distances [84]. IFEFFIT on the other hand assumes an \textit{a priori} structure consisting of nearest neighbor shells, which, due to multiple-scattering, may partially overlap (particularly beyond the second or third nearest neighbor) [62]. The IFEFFIT approach takes advantage of Fourier Transformations (FTs) to separate the various shell contributions and fit them individually to obtain their respective structural parameters.

4.1.1 The IFEFFIT software package

Figure 4.1 shows the structure of the IFEFFIT software package. IFEFFIT combines the algorithms of AUTOBK [85] and FEFFIT [86]. The former removes the atomic background from a measured EXAFS spectrum, while the latter algorithm fits the experimental EXAFS to theoretical calculations from FEFF [62].
IFEFFIT, though interactive, is a command-line program. However, there are several graphical user interfaces using the IFEFFIT library, including ATHENA and ARTEMIS, thus making the IFEFFIT fitting procedure easily accessible [87]. The main task of ATHENA is to use AUTOBK to extract the EXAFS signal, while ARTEMIS uses FEFF to fit the spectra.

![Diagram of IFEFFIT EXAFS analysis software structure](image)

Figure 4.1: Diagram of the IFEFFIT EXAFS analysis software structure. IFEFFIT uses the AUTOBK and FEFFIT algorithms. ATHENA and ARTEMIS are graphical user interfaces for IFEFFIT.

The IFEFFIT software package has been used for in this thesis, for the analysis of mono-elemental metallic nanoparticles and bulk standards (Zn and Cu) and variable temperature measurements (up to room temperature). The routines for extracting and fitting EXAFS data are explained in further detail in the following sections. No further reference to the specific programs are made.

## 4.2 Extraction of EXAFS

An example of a fluorescence mode x-ray absorption spectrum is shown in Figure 4.2 for a polycrystalline Cu foil at the K-edge at 12K. Such a spectrum is measured by a multi-element Ge solid state detector (the average scan, as shown, was
determined using standard software, while slight variations in individual element yield is taken care of by normalization). The monochromator is calibrated prior to the first measurement at a given edge (generally the first sample measured is the bulk standard). For example, the Cu K-edge energy calibration was performed with respect to the first peak after the edge, as indicated by the arrow in the Figure 4.2 inset. Subsequent scans are aligned to the bulk standard to account for monochromator drift (typically \( \leq 1 \text{ eV} \)). The edge step in Figure 4.2 has been normalized to enable comparison of the scattering yield between the various samples.

Figure 4.2: X-ray absorption spectrum for a polycrystalline Cu foil at the K-edge, measured in fluorescence mode at 12 K and (inset) the XANES region.
4.2. EXTRACTION OF EXAFS

4.2.1 Background subtraction

In order to extract structural information, it is necessary to separate the EXAFS oscillations, $\chi(E)$, from the measured absorption spectrum. We have defined $\chi$ previously (c.f. Equation 2.5) in terms of the absorption coefficient $\mu$:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$

(4.1)

where $\mu_0$ is the absorption coefficient of an “isolated” atom. This atom is embedded in the electronic environment of the condensed system, but without backscattering contributions from the near neighbors. The background function is a much more smoothly varying function than is the EXAFS (the former is proportional to $E^{-3}$ according to Equation 2.2). Extraction of the background is critical in the EXAFS analysis as this function can affect the final conclusions for the structural information [85].

Usually the background is approximated by a piecewise polynomial, or spline function [85]. Splines are particularly flexible mathematical expressions controlled by a number of knots where two polynomial segments join, and where discontinuity in the background derivative function is allowed. Background approximation is thus reduced to considering the conditions of the spline, including the polynomial order, number of knots and knot locations.

The spline function used for processing the data consisted of a number of fourth-order polynomials with knots equally separated in $k$-space. The number of knots is limited by the degrees of freedom for the system, which depends on the useful $k$-range [85] (typically 10 - 14 knots were used). The algorithm finds the spline which best eliminates the nonstructural components between the absorber and the first scatterer (equivalently the low-frequency components of the FT of the data are minimised) [85]. Figure 4.3 shows the measured absorption and the
background function determined for the polycrystalline Cu foil standard. The inset shows the isolated EXAFS oscillations as a function of energy.

![Measured x-ray absorption spectrum for a polycrystalline Cu foil including the background function and (inset) the isolated EXAFS modulations.](image)

**Figure 4.3:** Measured x-ray absorption spectrum for a polycrystalline Cu foil including the background function and (inset) the isolated EXAFS modulations.

### 4.3 Fourier Transformations

The isolated EXAFS, $\chi(E)$, is converted into a $k$-space function, $\chi(k)$, following Equation 2.6. Figure 4.4(a) shows the $\chi(k)$ function for polycrystalline Cu. There is a rapid decay of the $\chi$ amplitude with increasing $k$, related to the decay terms of the EXAFS equation (i.e. the limited mean free path and structural disorder terms of Equation 2.18). Commonly the $\chi(k)$ is $k$-weighted to emphasize the portion of interest of the spectrum. For example, the $k \times \chi(k)$, $k^2 \times \chi(k)$ and
4.3. FOURIER TRANSFORMATIONS

$k^3 \times \chi(k)$ are shown in Figures 4.4(b) through (d), respectively. The choice of $k$-weight for analysis purposes is determined by the quality of the data (useful $k$-range) and the type of absorbing and scattering elements. For example, for Cu measured at 12K a $k^3$-weighting was used, while Cu measured at elevated temperatures was weighted with $k^2$ due to the increased amount of (thermal) disorder and consequently a lesser usable $k$ range.

Figure 4.4: Isolated EXAFS modulations as a function of photoelectron momentum where (a) is the raw data and (b) through (d) are different $k$-weights.

Two FTs are applied to the data. The first is a forward FT applied to the $k$-weighted $\chi(k)$ data, which transforms the data into radial space. The second is
a backward FT to isolate a single scattering shell in \( k \)-space. The two FT steps are explained in detail below.

### 4.3.1 Forward Fourier Transformation

Given the limited EXAFS data range, typically \( k \in \langle 0, 20 \rangle \AA^{-1} \), application of a FT is not straightforward. To minimise truncation ripples, a symmetric windowing function is normally applied. An example of a forward FT window is shown in Figure 4.4(d). The window is a Hanning window, which was used throughout this thesis. The Hanning window features a constant value over about 80% of its width, while the edges are defined by \( \sin^2 \) and \( \cos^2 \) functions [57]. The lower bound of the window is limited by excitations into bound states (XANES) and multiple scattering. The lower \( k \)-limit is typically 3 – 4 Å (corresponding to 30 – 60 eV above the edge). The upper bound of the window is limited by the reduction in backscattering amplitude and associated relative increase in noise level. Typically, the upper limit was about 15 – 18 Å (860 – 1230 eV above the edge) for cryogenic temperature measurements, while elevated temperature measurements were limited to about 10 – 13 Å (380 – 640 eV above the edge).

Figure 4.5 shows the effect of \( k \)-weighting on the FT EXAFS data. The FT presents the atomic environment in conjugate \( r \)-space, where \( r \) is the radial distance from the absorber to the scatterer [57] (the phase shift contribution, typically \( \sim +0.3 \) Å, is not included). Thus, each of the peaks in Figure 4.5 represents atomic scattering shells (i.e. NN shells) with respect to the absorber. The first, second and third NNs for polycrystalline Cu are located at \( r \sim 2.3, 3.4 \) and 4.1 Å, respectively. A consistent fitting approach was always applied, i.e. the forward FT window and \( k \)-weight were kept constant for all samples, once the best conditions were determined.
Figure 4.5: Fourier Transformed (FT) EXAFS as a function of radial distance where (a) is the unweighted data and (b) through (d) are different $k$-weights.

4.3.2 Backward Fourier Transformation

Following forward FT, individual NN shells can be isolated, using a Hanning window, and backtransformed into $k$-space for quantitative analysis. Figure 4.6(a) shows the Hanning window used to separate the first NN, while the corresponding $k$-space function is compared with the complete $\chi(k)$ in (c). Clearly, the first NN corresponds to the main frequency present in the measured EXAFS data. For the latter, the superposition of scattering from all neighbors causes the signal to consist of multiple frequencies. Again, a consistent approach for
the backward transformation was always applied. The upper and lower limits for the window were chosen to best isolate the first NN, minimising the influence of the second NN. This is illustrated in Figure 4.6(b) where the Hanning window is superimposed on the two first theoretical FEFF paths. The window was always chosen to be symmetric about the NN. Once the optimum window conditions were determined, they were kept constant for the analysis of all samples.

4.4 Non-linear least-squares fit

Having isolated the scattering shell of interest, it must be compared with our knowledge of the theoretical scattering parameters (FEFF). Our chosen set of variables, \( x \), are optimised by a standard non-linear least-squares procedure [88]. The function to minimise, \( f(r, x) \), is given by:

\[
f(r, x) = FT[\chi_{\text{measured}}(k, x) - \chi_{\text{FEFF}}(k)]
\]

for \( r \) within the Hanning window. The best set of variables, \( x \), are those that minimise the sum of squares of the components of \( f(r, x) \). Some of these variables (such as \( S_0^2 \) and \( E_0 \)) can be determined from reference compounds, e.g. polycrystalline Cu, and fixed for the analysis of the samples of interest (e.g. Cu nanoparticles). The upper limit for the independent number of simultaneous fitting parameters, \( N_{idp} \), is given by a modified Nyquist criterion [89]:

\[
N_{idp} = \frac{2\Delta k \Delta r}{\pi} + 2
\]

where \( \Delta k \) and \( \Delta r \) are the widths of the forward and backward FT windows, respectively, i.e. the information content of the measured EXAFS data. Commonly, \( N_{idp} \geq 9 \), while the number of independent variables to be fitted is \( \sim 4 \) excluding \( S_0^2 \) and \( E_0 \) (determined from the standard for which the coordination number is
4.4. NON-LINEAR LEAST-SQUARES FIT

Figure 4.6: EXAFS data of polycrystalline Cu. The forward FT is shown in (a), including the Hanning window used to isolate the first nearest neighbor shell located at $\sim 2.3 \text{ Å}$, while in (b) the window is overlayed the two first theoretical FEFF paths. In (c), the backward transformation of the isolated first shell (black line) is compared to the measured EXAFS spectrum (grey line).
known). Careful analysis, including investigating the influence of $k$-weight, $\Delta k$, $\Delta r$, $S_0^2$, $E_0$, etc. is imperative as the disadvantage of the least-squares minimisation procedure is strong parameter correlation. For example, there is commonly a strong correlation between the coordination number and the Debye-Waller factor and between the bond length and the third cumulant. Thus, while seeking the global minimum several local minima, which must be avoided, may be sampled in the process.

Uncertainties for the $x$ variables are estimated in terms of a goodness-of-fit procedure [90]. Moving away from the estimated global minimum and corresponding best fit parameters, the minimised function $f(r, x)$ will increase. Imposing a limit on how far away it is reasonable to move [90], uncertainties can be evaluated for the reported parameters. Parameter correlation is thus a measure of how much the best-fit value of one of the variables changes in response to changing another variable away from its best-fit value.

### 4.4.1 Radial distribution functions

The structural parameters of a system are best represented visually by the RDF. Note that the forward FT EXAFS, e.g. Figure 4.6(a), should not be interpreted as the RDF given (1) the lack of the phase shifts in the FT, which depend on both absorbing and scattering atom types, (2) multiple scattering paths can produce peaks in the FT, (3) interference between paths can lead to non-physical minima and maxima in the FT and (4) the FT amplitude depends on the photoelectron scattering factor as well as the radial distribution of atomic distances, while a RDF does not depend on the photoelectron scattering factors.
The real RDF, $\rho(r)$, is given by [61]:

$$\rho(r) = \frac{r^2 N_s}{R_s^2} \exp[2\Delta r / \lambda] \int_0^\infty \chi'(|k|) \sin(2k\Delta r) dk$$

where $r$ is the distance, $N_s$ is the reference coordination number, $R_s$ is the reference average distance, $\Delta r$ is the distance difference between the sample (e.g. Cu nanoparticles) and the reference (e.g. bulk Cu), $\lambda$ is the mean free path and $\chi'(|k|)$ is the cumulant expansion of the EXAFS Debye-Waller term (Equation 2.12). The strict limits for the integral are not achievable in EXAFS measurements given the limitations at low and high $k$ as discussed previously. However, utilizing the cumulant method, where the amplitudes and phases of a sample are compared to the appropriate standard [91], the data can be extrapolated down to $k=0$ and up to a value for $k$ where the cumulant series converges. Thus, Equation 4.4 is simplified [91] to:

$$\rho(r) \approx \frac{r^2 N_s}{R_s^2} \exp[2\Delta r / \lambda] \int_0^{k_{up}} \chi'(|k|) \sin(2k\Delta r) dk$$

where $k_{up}$ is the value of $k$ for which the series converges. Not knowing the precise value of $\lambda$ introduces only small errors, since typically $\lambda \approx 8\text{Å}$ while $\Delta r \leq 0.5\text{Å}$ [61].

The cumulants, $C_n$ ($n=0,1,2,\ldots$), have simple interpretations in terms of the distribution of interatomic distances [91], where $C_0$ depends on the normalization of the distribution, $C_1$ represents the mean value, $C_2$ the variance, $C_3$ (and higher order odd cumulants) the asymmetric deviations from a Gaussian distribution, and $C_4$ (and higher order even cumulants) represents the symmetric deviations from a Gaussian distribution. Thus if $C_{n\geq3} = 0$, the distribution is Gaussian. (For the work presented in this thesis cumulants up to third order ($n=3$) were used, while fourth order and above were not required.)
Figure 4.7 shows the influence of varying the first three cumulants with respect to a Gaussian reference distribution. In Figure 4.7(a) a $C_1$ offset is applied, which simply moves the Gaussian closer to or further away from the central atom. In Figure 4.7(b) a $C_2$ offset is applied, which changes the full width half maximum of the Gaussian. Finally, in Figure 4.7(c) a $C_3$ is introduced. The distribution is markedly non-Gaussian, i.e. skewed towards shorter radial distances for a positive $C_3$ and towards longer radial distances for a negative $C_3$. In both cases the average distance is the same.

4.5 Summary

This chapter has presented and discussed the EXAFS analysis procedures used in this thesis. In general terms the procedure can be summarized as follows: (1) the EXAFS modulations are isolated from the raw absorption spectrum, (2) an appropriate forward FT window is applied to extract the $r$-dependent scattering spectrum, (3) an appropriate backward FT window is applied to isolate the first NN, which is then (4) compared with the theoretical standard, from which structural parameters for that shell may be extracted.

The following chapter presents the results and discussions on ion beam synthesized Cu nanoparticles.
Figure 4.7: Reconstructed radial distribution functions (RDFs). The black spectrum is a reference Gaussian curve with $C_1 = 2.5 \text{Å}$, $C_2 = 2.5 \times 10^{-3} \text{ Å}^2$ and $C_3 = 0$. The mean free path and the coordination number were 8Å and 12 atoms, respectively, throughout. In (a) the red curve has $C_1$ offset by -0.05Å, while the blue curve has $C_1$ offset by +0.05Å. In (b) the red curve has $C_2$ offset by -0.5$\times10^{-3}$Å$^2$, while the blue curve has $C_2$ offset by +0.5$\times10^{-3}$Å$^2$. In (c) the red curve has $C_3$ offset by -1$\times10^{-4}$Å$^3$, while the blue curve has $C_3$ offset by +1$\times10^{-4}$Å$^3$. 
CHAPTER 4. EXAFS DATA ANALYSIS

Chapter 5

Formation of Cu Nanoparticles

This chapter discusses the formation of Cu nanoparticles in aqueous 50% as a function of synthesis parameters, including the employed Cu concentrations and thermal annealing temperature. The significant fraction of nanoparticles nucleate around the measured structural parameters to deviate from those of the bulk counterpart. Depending on the synthesis conditions, a significant fraction of Cu-O bonds was also observed. The bond coordination of Cu-O in these nanoparticles was comparable to that of a bulk CuO standard, albeit not in a crystalline form. The surface tension of Cu nanoparticles was estimated to be greater than that of the corresponding Cu nanoparticles, indicating the influence of the host matrix. Moreover, from temperature-dependent EXAFS measurements, smaller nanoparticles (3.5 nm) exhibited thermal characteristics different from those of the bulk counterpart, while larger nanoparticles (11.0 nm) did not show appreciable differences.
Chapter 5

Formation of Cu Nanoparticles

This chapter discusses the formation of Cu nanoparticles in amorphous SiO₂ as a function of synthesis parameters, including the implanted Cu concentration and thermal annealing temperature. The significant fraction of nanoparticle surface atoms caused the measured structural parameters to deviate from those of the bulk counterpart. Depending on the synthesis conditions, a significant fraction of Cu-O bonds was also observed. The local coordination of the O-rich environment was comparable to that of a bulk Cu₂O standard, albeit not in a crystalline form. The surface tension of Cu nanoparticles was estimated to be greater than that of freestanding Cu nanoparticles, indicating the influence of the host matrix. Meanwhile, from temperature dependent EXAFS measurements, small nanoparticles (3.3 nm) exhibited thermal characteristics differing from those of the bulk counterpart, while larger nanoparticles (14.0 nm) did not show appreciable differences.
5.1 Introduction

In the present chapter, Cu nanoparticles were synthesized in amorphous silica (SiO$_2$) by high energy ion implantation and subsequent thermal annealing. Others have previously used EXAFS to study Cu nanoparticles embedded in SiO$_2$ [92, 93], in other hosts [25, 94] and in an unsupported form [95]. Due to the finite size of nanoparticles and their under-coordinated surface atoms, the average coordination number, measured by EXAFS, is suppressed compared to that of the bulk standard (12 atoms). Assuming a face-centred cubic (fcc) Cu structure, the average coordination number is expected to be less than 11 atoms only for nanoparticles smaller than about 5 nm in diameter [22]. Similarly, theoretical variations in the interatomic distances calculated for fcc Cu nanoparticles are negligible for diameters larger than 5 nm [25]. Experimentally, relatively large unsupported Cu nanoparticles (10 - 20 nm diameter) have been reported to retain the Cu-Cu bond length and show a marginal reduction in coordination number relative to bulk standards [95]. The presence of a supporting matrix and nanoparticle atoms bonding to this material may enhance disorder to yield structural deviations in nanoparticles of diameters exceeding 5 nm. For example, polyethylene-supported Cu nanoparticles (13 - 17 nm diameter) exhibit a reduced bond length [94], while SiO$_2$ supported Cu nanoparticles of significantly smaller diameters (3.8 - 7.8 nm) reportedly retain the bulk bond length, while the coordination is suppressed [92] to a greater extent than expected theoretically [22]. The latter observation was attributed to the presence of an oxidized phase. Cu clusters (0.7 - 1.5 nm diameter) embedded in solid Ar were reported with significantly reduced bond length and coordination number [25].

The present study seeks a better understanding of the influence of the processing parameters on the structure of Cu nanoparticles. Both the implantation
fluence and annealing temperature dependence of Cu nanoparticle formation utilizing ion beam synthesis will be presented. Deviations in coordination number and bond length are measured and attributed to either the presence of an oxidized phase or structural disorder. Previous reports of EXAFS measurements on Cu nanoparticles have typically been limited to a photoelectron wave vector \( (k) \) maximum of \( \sim 12 \text{ Å}^{-1} \), yielding bond length estimations to within 0.01 Å [92]. In the present report the \( k \) range is extended to 18 Å\(^{-1}\), which improves the structural parameter resolution and enables analysis of the third cumulant [96] (the asymmetric deviation from a Gaussian interatomic bond length distribution). Thermal characteristics of representative samples were also investigated with temperature dependent EXAFS measurements.

5.2 Experimental

Nanoparticle formation

5 \( \mu \text{m} \) SiO\(_2\) films, grown on Si(100) substrates by wet thermal oxidation, were implanted at a range of energies with \(^{63}\)Cu ions as listed in Table 5.1. For the lower fluence samples multiple energy implantations were performed to increase the effective EXAFS yield, without increasing the peak Cu concentration as compared to the highest fluence sample. The peak Cu concentration in the samples was between 0.3 and 8.6 at.%. All implantations were performed at liquid nitrogen temperature to minimise ion beam induced diffusion. Shown in Figure 5.1 are the implantation profiles as calculated with the TRIM code [16]. All samples were implanted to a Cu concentration in excess of the solubility limit for Cu in SiO\(_2\) (< 10\(^{12}\) cm\(^{-3}\) at room temperature [97]). Following implantation, samples were annealed in flowing forming gas (5% H\(_2\) in N\(_2\)) for 1 h at temperatures of 500,
800 and 1100 °C to induce Cu precipitation and nanoparticle growth [98].

Table 5.1: Summary of the Cu ion implantation parameters. The implantation range and the Cu concentration values are based on results from the TRIM code [16].

<table>
<thead>
<tr>
<th>Fluence (cm(^{-2})) implanted at energy E (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E=800</td>
</tr>
<tr>
<td>6.4x10(^{15})</td>
</tr>
<tr>
<td>1.9x10(^{16})</td>
</tr>
<tr>
<td>8.3x10(^{16})</td>
</tr>
<tr>
<td>3.0x10(^{17})</td>
</tr>
</tbody>
</table>

Nanoparticle characterization

RBS was performed using 4.2 MeV He\(^{2+}\) ions. This enabled investigation of the implantation profile to a depth of ~2 µm to probe the Cu concentration before and after thermal annealing. Conventional XRD was used to identify the structural phase of the nanoparticle samples and estimate their average size using the Scherrer formula [67]. Measurements were performed with the sample surface oriented at a glancing incident angle of 2 ° with respect to the x-ray beam. Cross-sectional TEM analysis was performed to enable quantitative examination of the nanoparticle size and depth distributions.

EXAFS spectroscopy was utilized to determine the bond length, coordination number, Debye-Waller factor and the third cumulant of the interatomic distance distribution. Measurements were performed in fluorescence mode at the Cu
Figure 5.1: Predicted implantation depth profiles of samples implanted to Cu concentrations of 0.3, 1.0, 3.2 and 8.6 at.%, respectively.

K-edge (8.979 keV). All samples were measured at a minimum achievable temperature of 15K (liquid He sample environment) to minimise thermal disorder. Selected samples were also measured at elevated temperatures (up to room temperature) to investigate thermal characteristics. EXAFS samples were prepared using the standard technique as illustrated in Figure 3.15. Fluorescence spectra were recorded for both nanoparticle samples and the reference compounds. The latter comprised of bulk polycrystalline Cu with grain size ~ 300 nm, bulk CuO powder and bulk Cu$_2$O powder. The Cu areal density of all standards was diluted to the value of the Cu nanoparticle samples to inhibit self-absorption. For both standards and nanoparticle samples, the Cu K-edge fluorescence signal comprised 30 - 60% of the incoming count rate, the latter maintained at < 60 000 counts/s.
(or equivalently within the linear counting regime with a shaping time of 0.5 $\mu$s). Fluorescence spectra were recorded to $k = 18 \text{ Å}^{-1}$ at 15K, while 15 $\text{Å}^{-1}$ sufficed for the temperature dependent study given the increase in disorder.

SAXS measurements were performed in transmission mode to investigate nanoparticle size distributions and were thus complementary to XRD and TEM results. The SAXS samples were the same as those used for EXAFS to ensure consistency and were measured at room temperature using 1.50 Å x-rays at normal incidence.

### 5.3 Results and discussion

#### 5.3.1 RBS, XRD and TEM

Figure 5.2 shows the RBS spectra for the 1.0 at.% Cu samples as a function of annealing temperature. Comparing the as-implanted and 500 °C sample, no redistribution of Cu was apparent (at depths 0 - 2 μm), and the depth profiles are consistent with those simulated by TRIM (Figure 5.1). At higher temperatures, loss of Cu can be inferred. At 800 °C a prominent Cu peak is observed at or near the SiO$_2$ surface, while at 1100 °C loss of Cu is apparent throughout the probed region of the implanted depth. The same trend was observed in the 0.3 at.% samples (with a complete loss of Cu after annealing at 1100 °C). Meanwhile, negligible loss was observed in the 3.2 and 8.6 at.% samples at any annealing temperature. The loss of Cu is attributed to evaporation and/or diffusion beyond the SiO$_2$/Si interface. Note that Cu is extremely mobile in SiO$_2$ with a diffusivity of ~ 50 μm$^2$/s at 730 °C in forming gas [97]. Similar observations have been reported by Umeda et al [99] and Nakao et al [100]. Samples with a high Cu concentration already contain a large number of nanoparticles prior to annealing (as apparent from TEM results discussed below). Upon annealing large nanoparticles grow at
Figure 5.2: RBS spectra for the 1.0 at.% Cu samples.

The expense of small ones and Cu atoms dissolved in the SiO₂ matrix. On the other hand, in samples with a low Cu concentration, there are fewer precipitation sites (such as matrix defects) after implantation, and upon annealing the dissolved Cu atoms may diffuse out of, or evaporate from, the implanted matrix.

Figure 5.3 shows the XRD spectra for the 3.2 at.% samples as a function of annealing temperature, including as a reference the spectrum for the bulk polycrystalline standard (scaled for comparison). With increasing annealing temperature we observe diffraction peaks emerging at angles of 50.9° and 59.3° (the latter not shown), corresponding to the (111) and (200) crystallographic planes, respectively, in fcc Cu. This trend is representative for all concentrations. Moreover, peak broadening decreased with increasing concentration and annealing temperature. The peak broadening reflects finite-size effects and/or disorder.
In order of (111) decreasing intensity:
- bulk Cu standard
- 1100°C
- 800°C
- 500°C
- as-implanted

![XRD spectra for the 3.2 at.% Cu samples. The bulk polycrystalline Cu standard spectrum is scaled for comparison.](image)

Figure 5.3: XRD spectra for the 3.2 at.% Cu samples. The bulk polycrystalline Cu standard spectrum is scaled for comparison.

(quantified by EXAFS measurements below) in the nanoparticle material. The average nanoparticle diameter can be approximated from the peak width. The full width half maximum (FWHM) of the most prominent nanoparticle diffraction peak was deconvoluted with that of the standard to isolate the size-related broadening. The Scherrer formula [67] was then applied to estimate the average nanoparticle diameter $D$:

$$D = \frac{0.9\lambda}{W \cos \theta}$$  \hspace{1cm} (5.1)

where $\lambda$ is the radiation wavelength, $W$ is the deconvoluted FWHM and $\theta$ is the Bragg angle. Results from the analysis performed using the (111) peak are listed in Table 5.2. The trend indicates an increase in nanoparticle size and/or a decrease in disorder with an increase in both concentration and annealing tem-
Table 5.2: Estimates of average nanoparticle diameters (nm) based on XRD analysis (n/m = not measurable).

<table>
<thead>
<tr>
<th>Cu conc. (at.%)</th>
<th>Annealing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as-impl.</td>
</tr>
<tr>
<td>8.6</td>
<td>13.8 ± 2.0</td>
</tr>
<tr>
<td>3.2</td>
<td>n/m</td>
</tr>
<tr>
<td>1.0</td>
<td>n/m</td>
</tr>
<tr>
<td>0.3</td>
<td>n/m</td>
</tr>
</tbody>
</table>

temperature. The TEM and EXAFS measurements presented below show that both factors are operative.

Figures 5.4 (a) and (b) show representative TEM micrographs of the 8.6 at.% samples as-implanted and annealed at 1100 °C, respectively. The TEM micrographs provided both qualitative and quantitative information of nanoparticle formation and shape. The nanoparticles were spherical and single crystalline for all concentrations and annealing temperatures. Electron diffraction patterns (not shown) confirmed the fcc structure, consistent with XRD results. The Figure 5.4(a) inset shows a high resolution image of an individual nanoparticle where the (111) lattice planes of fcc Cu are discernable. The lattice spacing was estimated to be 2.08 ± 0.09 Å in good agreement with the listed nominal value of 2.088 Å [101]. Figures 5.4 (c) and (d) show the corresponding size distributions evaluated from the micrographs covering the extent of the implantation range. Average nanoparticle diameters were calculated by averaging over the nanoparticle volume through cubic weighting of the extracted nanoparticle diameters. This allows
Figure 5.4: TEM micrographs of Cu nanoparticles: (a) 8.6 at.% as-implanted, (b) 8.6 at.% 1100°C and respective size distributions in (c) and (d). The mean volume averaged nanoparticle diameters are indicated by the dashed lines. Inset in (a) is a representative single crystalline nanoparticle where the (111) lattice planes are discernible.
for direct comparison with the EXAFS measurements, being a volume-weighted technique. The size distributions are relatively wide, with a FWHM of ~ 6 nm, characteristic of ion beam synthesized nanoparticle ensembles [102]. Table 5.3 summarizes the average nanoparticle diameter extracted from TEM analysis. The results agree, within experimental errors, with those obtained from XRD analysis (Table 5.2) considering finite-size effects only.

Table 5.3: Estimates of average nanoparticle diameters (nm) based on TEM analysis (n/m = not measurable).

<table>
<thead>
<tr>
<th>Cu conc. (at.%)</th>
<th>Annealing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6 14.1 ± 3.0</td>
<td>15.2 ± 3.0</td>
</tr>
<tr>
<td>3.2 n/m</td>
<td>14.9 ± 3.0</td>
</tr>
<tr>
<td>1.0 n/m</td>
<td>14.6 ± 3.0</td>
</tr>
<tr>
<td>0.3 n/m</td>
<td>no Cu</td>
</tr>
</tbody>
</table>

5.3.2 EXAFS spectra, Fourier transforms and XANES

Figure 5.5 displays $k^2$-weighted EXAFS spectra measured for different annealing temperatures comparing the 1.0 at.\% Cu samples with the bulk Cu standard. These results offer significantly improved statistics compared to previous reports [93, 92]. In general, the EXAFS amplitude increases with increasing annealing temperature, consistent with nanoparticle formation and growth. This trend was also observed for other concentrations, though for the 8.6 at.\% samples the variation was minimal relative to the bulk Cu standard. For this Cu concentration, this
Figure 5.5: EXAFS spectra of 1.0 at.% implanted samples as compared to that of the bulk Cu standard. The spectra are shifted for clarity.

indicates negligible nanoparticle size growth with annealing temperature and/or formation of nanoparticles in the as-implanted stage of sufficient average diameter to exhibit insignificant structural deviations with respect to the bulk standard. No EXAFS was measurable for the 0.3 at.% sample annealed at 1100 °C, consistent with the absence of Cu apparent from RBS results. Figure 5.6 shows the Fourier transforms (FTs) corresponding to the spectra in Figure 5.5 as a function of the radial distance (using a $k$-window of $4.0 - 17$ Å$^{-1}$). The three first nearest neighbor shells of Cu are observed at phase-corrected radial distances of $\sim 2.5$, 3.6 and 4.3 Å, respectively. In general, the nanoparticle samples exhibited a reduced amplitude with respect to the bulk, indicating higher structural disorder and/or lower coordination number. With increasing annealing temperature,
the amplitudes increase. As discussed previously, these results are consistent with annealing-temperature-dependent nanoparticle nucleation and growth. The same trend was observed for the remaining concentrations as functions of annealing temperature, again with the exception of the 8.6 at.% samples. Moreover, a concentration dependence was observed with an increase in amplitude with increasing concentration.

Any contributions to the FT, above noise level and between the Cu absorber and the first nearest neighbor Cu scatterers, arise from atoms bonding to Cu with a shorter bond length, typically O. Such contributions are apparent for the as-implanted and 500 °C samples in Figure 5.6 (inset), at a radial distance between
~ 1 - 2 Å, where the Cu-O contribution is appreciable compared to the Cu-Cu signal. In general, samples of low concentration and/or low annealing temperature exhibited a significant Cu-O scattering contribution. Such samples thus contain Cu oxides (CuO or Cu₂O) and/or partially oxidized Cu nanoparticles. Figure 5.7 compares the XANES spectra of bulk Cu, CuO and Cu₂O standards with a selection of Cu nanoparticle samples. The Cu K-edge of CuO exhibits a chemical shift to higher energy [103], while Cu₂O has a prominent pre-edge feature and negligible edge shift. Note that the XANES of the 0.3 and 1.0 at.% as-implanted samples are comparable to the Cu₂O spectrum, in contrast with that of CuO. We can infer from XANES that Cu atoms dissolved in the matrix and/or partially oxidized nanoparticles, prefer a square coordination of O atoms in the first shell (as in Cu₂O). This agrees with previous reports on embedded Cu nanoparticles [104] and also bulk Cu has been reported to primarily form Cu₂O when exposed to atomic O [105]. In summary, XANES measurements demonstrated that both as-implanted samples (0.3, 1.0 and 3.2 at.%) and samples annealed at 500 °C (0.3 and 1.0 at.%) contained a significant fraction of oxidized Cu atoms with an oxidation state similar to that in Cu₂O (albeit not in a crystalline form as shown below).

### 5.3.3 Analysis of Cu-Cu and Cu-O bonding

Structural parameters, including the coordination number, bond length, Debye-Waller factor and third cumulant, were extracted by isolating the first nearest neighbor Cu shell over a non-phase-corrected radial distance in the range of 1.62 - 2.88 Å. Table 5.4 summarizes the results of the Cu-Cu analysis. For comparison, the average nanoparticle diameter, determined by XRD and TEM analysis is included.
Table 5.4: Structural parameters of bulk Cu and Cu nanoparticles as extracted by first nearest neighbor Cu shell EXAFS analysis ($k^2$-weighted). Legend: CN = coordination number, BL = bond length, DW = Debye-Waller factor, C3 = third cumulant, n/m = not measurable, * = significant Cu-O EXAFS signal. The measured coordination number has not been corrected for the fraction of Cu-O bonding.

<table>
<thead>
<tr>
<th>Cu-Cu analysis</th>
<th>CN (atoms)</th>
<th>BL (Å)</th>
<th>DW ($10^{-3}$ Å²)</th>
<th>C3 ($10^{-5}$ Å³)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Cu standard</td>
<td>12 (fixed)</td>
<td>2.539 ± .001</td>
<td>2.45 ± .04</td>
<td>n/m</td>
<td>–</td>
</tr>
<tr>
<td>8.6 at.%, as-impl.</td>
<td>10.8 ± .2</td>
<td>2.538 ± .001</td>
<td>2.71 ± .09</td>
<td>-4.3 ± 1.2</td>
<td>13.9 ± 1.7</td>
</tr>
<tr>
<td>8.6 at.%, 500 °C</td>
<td>10.6 ± .3</td>
<td>2.538 ± .001</td>
<td>2.85 ± .10</td>
<td>-4.3 ± 1.3</td>
<td>12.5 ± 2.0</td>
</tr>
<tr>
<td>8.6 at.%, 800 °C</td>
<td>12.1 ± .3</td>
<td>2.538 ± .002</td>
<td>2.53 ± .11</td>
<td>-6.4 ± 1.4</td>
<td>15.5 ± 2.0</td>
</tr>
<tr>
<td>8.6 at.%, 1100 °C</td>
<td>12.4 ± .4</td>
<td>2.540 ± .002</td>
<td>2.45 ± .12</td>
<td>-2.4 ± 1.6</td>
<td>15.4 ± 1.7</td>
</tr>
<tr>
<td>3.2 at.%, as-impl.*</td>
<td>4.2 ± .4</td>
<td>2.529 ± .015</td>
<td>3.37 ± .51</td>
<td>-22.4 ± 13.3</td>
<td>n/m</td>
</tr>
<tr>
<td>3.2 at.%, 500 °C</td>
<td>6.8 ± .9</td>
<td>2.531 ± .008</td>
<td>3.63 ± .67</td>
<td>-8.7 ± 4.4</td>
<td>9.0 ± 2.0</td>
</tr>
<tr>
<td>3.2 at.%, 800 °C</td>
<td>10.6 ± .4</td>
<td>2.532 ± .002</td>
<td>3.41 ± .17</td>
<td>-4.1 ± 2.3</td>
<td>12.0 ± 2.0</td>
</tr>
<tr>
<td>3.2 at.%, 1100 °C</td>
<td>12.3 ± .5</td>
<td>2.541 ± .002</td>
<td>2.46 ± .17</td>
<td>-0.9 ± 2.2</td>
<td>13.9 ± 1.7</td>
</tr>
<tr>
<td>1.0 at.%, as-impl.*</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
</tr>
<tr>
<td>1.0 at.%, 500 °C*</td>
<td>4.3 ± .6</td>
<td>2.509 ± .016</td>
<td>5.20 ± .86</td>
<td>-15.4 ± 16.5</td>
<td>n/m</td>
</tr>
<tr>
<td>1.0 at.%, 800 °C</td>
<td>10.6 ± .5</td>
<td>2.525 ± .003</td>
<td>4.12 ± .22</td>
<td>-6.6 ± 3.0</td>
<td>n/m</td>
</tr>
<tr>
<td>1.0 at.%, 1100 °C</td>
<td>13.5 ± 1.1</td>
<td>2.541 ± .003</td>
<td>2.82 ± .27</td>
<td>-3.5 ± 3.1</td>
<td>14.5 ± 1.7</td>
</tr>
<tr>
<td>0.3 at.%, as-imp.*</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
</tr>
<tr>
<td>0.3 at.%, 500 °C*</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, CN &lt; 1</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
</tr>
<tr>
<td>0.3 at.%, 800 °C</td>
<td>10.3 ± .9</td>
<td>2.515 ± .005</td>
<td>4.32 ± .43</td>
<td>-19.1 ± 5.8</td>
<td>n/m</td>
</tr>
<tr>
<td>0.3 at.%, 1100 °C</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
<td>n/m, only traces of Cu remained in sample after annealing</td>
</tr>
</tbody>
</table>
Figure 5.7: XANES spectra of bulk Cu, CuO, and Cu$_2$O standards as compared to a selection of Cu nanoparticle samples. The spectra are shifted for clarity.

Table 5.4 lists a total of five samples where a significant Cu-O EXAFS signal was detected, in accordance with Figures 5.6 and 5.7. For these samples, an O shell was fitted and compared to the first nearest neighbor O shell for the Cu$_2$O standard. Since O is a low-Z scatterer, $k^3$-weighting was applied to emphasize
Table 5.5: Structural parameters of bulk Cu and oxidized Cu nanoparticles as extracted by first nearest neighbor O shell EXAFS analysis. Legend: CN = coordination number, BL = bond length, DW = Debye-Waller factor. The measured coordination number has not been corrected for the fraction of Cu-Cu bonding.

<table>
<thead>
<tr>
<th>Cu-O analysis</th>
<th>CN</th>
<th>BL</th>
<th>DW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(atoms)</td>
<td>(Å)</td>
<td>(10^{-3} Å²)</td>
</tr>
<tr>
<td>Bulk Cu₂O standard</td>
<td>2 (fixed)</td>
<td>1.83 ± .01</td>
<td>2.0 ± .8</td>
</tr>
<tr>
<td>3.2 at.%, as-impl.</td>
<td>1.1 ± .3</td>
<td>1.76 ± .02</td>
<td>3.9 ± 2.7</td>
</tr>
<tr>
<td>1.0 at.%, as-impl.</td>
<td>2.1 ± .4</td>
<td>1.75 ± .01</td>
<td>5.6 ± 3.4</td>
</tr>
<tr>
<td>1.0 at.%, 500 °C</td>
<td>1.0 ± .2</td>
<td>1.77 ± .04</td>
<td>5.5 ± 6.4</td>
</tr>
<tr>
<td>0.3 at.%, as-impl.</td>
<td>2.8 ± .5</td>
<td>1.75 ± .01</td>
<td>7.6 ± 3.6</td>
</tr>
<tr>
<td>3.2 at.%, 500 °C</td>
<td>2.1 ± .4</td>
<td>1.82 ± .01</td>
<td>5.1 ± 2.2</td>
</tr>
</tbody>
</table>

the Cu-O bonds and better define the Cu-O parameters. Table 5.5 summarizes the results of the Cu-O analysis. The results are consistent with XANES analysis presented above, which showed that oxidized Cu was present with similar oxidation state and local coordination as that of Cu₂O (with 2 O atoms in its first shell). Nonetheless, the increased Debye-Waller factor indicates that oxidized Cu is present in a far more disordered form than crystalline Cu₂O.

In the presence of two environments (Cu-Cu and Cu-O), the measured Cu-Cu and Cu-O coordination numbers are both reduced. For example, a Cu atom bonding to O will contribute to the absorption (which is normalized), but not to the Cu-Cu coordination number. Similarly, a Cu atom bonding to Cu will
also contribute to the absorption, but not to the Cu-O coordination number. In Table 5.5, a partial Cu-O coordination number of \(~2\) atoms (as in the standard) was measured in three samples, indicating that a Cu-O environment is dominant. This is consistent with the lack of Cu-Cu scattering (Table 5.4). For the remaining two samples listed in Table 5.5, a partial Cu-O coordination number of \(~1\) is reported. Given the argument above, that both environments contribute to the total absorption, both the measured Cu-O and Cu-Cu coordination number for these two samples are likely to be smaller than the real coordination number. With an appropriate Cu silicate standard, XANES analysis could be further utilized to quantify the fractions in oxidized and metallic forms [92].

Apparent from Tables 5.4 and 5.5, and as expected, the O coordination number decreases with increasing Cu concentration and annealing temperature, while a concurrent increase in the Cu coordination number is measured. The O coordination number decreases to insignificant values as the Cu coordination number increases beyond four indicating an increasing average nanoparticle diameter and/or a decreasing fraction of Cu dissolved in the matrix.

### 5.3.4 Summary of the extracted structural parameters

The Cu-Cu analysis summarized in Table 5.4 reveals a concentration- and annealing-temperature dependence in all structural parameters, as observed qualitatively in the Fourier transformed spectra of Figure 5.6. In general, both a suppressed coordination number and decreased bond length is apparent together with an increased Debye-Waller factor and negative third cumulant term. Figures 5.8(a) through (d) show the concentration- and annealing-temperature dependence of all four parameters. We note that for all samples annealed at 1100 °C, these parameters are comparable to those of the bulk Cu standard, indicative of the relatively
Figure 5.8: Concentration- and annealing-temperature dependence of four structural parameters in Cu nanoparticle samples as compared to the bulk Cu standard: (a) coordination number, (b) bond length, (c) Debye-Waller factor, (d) third cumulant.
large average size of nanoparticles in these samples. The decrease in the average coordination number for lower concentrations and annealing temperatures is a result of the significantly lower coordination state of the surface atoms and the presence of oxides [92]. The increase in the Debye-Waller factor is consistent with surface reconstruction and/or disorder. For the as-implanted and 500 °C samples (8.6 and 3.2 at.%) the Debye-Waller factor is slightly larger than at the higher annealing temperatures. This is potentially related to the host imposing pressure on the nanoparticles below the viscosity limit of SiO₂ [34]. The negative value for the third cumulant observed in all nanoparticle samples indicates a bond length distribution skewed towards shorter bond lengths. This might be explained by the reconstruction of the surface atoms involving a shortened bond length.

For those samples where the nanoparticle size was measured by XRD/TEM (Tables 5.2 and 5.3), results have been superimposed onto a theoretical plot for the size-dependent coordination numbers in Figure 5.9. The theoretical curve (solid line) assumes fcc Cu [22]. We observe a deviation from theory for the 3.2 at.% sample annealed at 500 °C, most likely due to the presence of Cu in an oxidized form, which, as discussed above, artificially lowers the measured coordination number.

The relative influences of the concentration- and annealing-dependent parameters are most apparent in the radial distribution function (RDF). The RDFs were reconstructed from the first three cumulants of the interatomic distance distribution following the method of Dalba and Fornasini [91] and using a photoelectron mean free path of 6 Å. Figure 5.10 compares the reconstructed RDFs for the first nearest neighbor shell in nanoparticle samples (annealed at 800 °C) to that of the bulk Cu standard. We note that with decreasing dose, or alternatively decreasing nanoparticle size, the distribution becomes increasingly asymmetric.
Figure 5.9: Average coordination number in the first nearest neighbor shell as a function of nanoparticle diameter.
Figure 5.10: Reconstructed radial distribution function of the first nearest neighbor shell for Cu nanoparticle samples at all concentrations (annealed at 800 °C) as compared to that of the bulk Cu standard.
and highlights the increasing importance of the under-coordinated surface atoms.

### 5.3.5 Size dependent structural disorder

Those samples where the implanted Cu is present in the form of nanoparticles (excluding those samples determined to contain a fraction of oxides, see Table 5.4) were measured with SAXS. Figure 5.11(a) shows SAXS intensities as a function of the scattering vector for two of these samples, while (b) and (c) show the resulting volume-weighted size distributions. The result presented in Figure 5.11(b) is in qualitative agreement with the size distribution as extracted by TEM analysis (c.f. Figure 5.4(d)).

Table 5.6 summarizes the obtained SAXS results. The EXAFS measured bond length contraction and increase in Debye-Waller factor (as compared to the bulk standard) are included. The sizes listed are comparable to those listed in Table 5.4 (based on XRD and TEM results), although some differences can be found. The latter can reflect the influence of a non-uniform sample thickness (TEM) and stress related peak broadening (XRD). As expected, Table 5.6 indicates a general increase in disorder and decrease in bond length with decreasing nanoparticle size.

Recent simulations of unsupported metallic nanoparticles suggest they are comprised of three regions: a structurally distorted surface shell and transition shell, and a bulk-like core region [23]. The surface and transition shells together account for the outer $\sim 5$ Å layer, which is independent of the system size. When this layer is comparably thin, as compared with the entire nanoparticle radius, it may be approximated by a two-dimensional entity. Hence the ratio of atoms in the outer shell to atoms in the bulk (that is a surface-to-volume ratio) is proportional to the inverse nanoparticle diameter [23]. Figure 5.12 shows (a) the bond
Figure 5.11: SAXS data and nanoparticle size distribution analysis: (a) SAXS data of 8.6 at.% (1100 °C) and 1.0 at.% (800 °C) with the scattering contribution of the SiO₂ subtracted. The volume-weighted nanoparticle size distributions are shown in (b) and (c), respectively.
Table 5.6: Summary of SAXS and EXAFS analysis of Cu nanoparticles as compared to a bulk Cu reference. The bond length (BL) contraction and increase in Debye-Waller factor (DW) in the Cu nanoparticles are relative to the absolute values for the bulk Cu standard. Note that the last entry is that for the unirradiated Cu nanoparticles discussed in Chapter 7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (nm)</th>
<th>BL (Å)</th>
<th>DW (10^{-3} Å^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Cu standard</td>
<td>-</td>
<td>2.539 ± 0.001</td>
<td>2.45 ± 0.04</td>
</tr>
<tr>
<td>8.6 at.%, as-impl.</td>
<td>15.2 ± 0.7</td>
<td>0.001 ± 0.001</td>
<td>0.26 ± 0.10</td>
</tr>
<tr>
<td>8.6 at.%, 500 °C</td>
<td>13.1 ± 0.5</td>
<td>0.001 ± 0.001</td>
<td>0.40 ± 0.11</td>
</tr>
<tr>
<td>8.6 at.%, 800 °C</td>
<td>14.0 ± 0.5</td>
<td>0.001 ± 0.002</td>
<td>0.08 ± 0.12</td>
</tr>
<tr>
<td>8.6 at.%, 1100 °C</td>
<td>22.9 ± 0.9</td>
<td>-0.001 ± 0.002</td>
<td>0.00 ± 0.13</td>
</tr>
<tr>
<td>3.2 at.%, 800 °C</td>
<td>7.2 ± 0.3</td>
<td>0.007 ± 0.002</td>
<td>0.96 ± 0.17</td>
</tr>
<tr>
<td>3.2 at.%, 1100 °C</td>
<td>13.4 ± 0.5</td>
<td>-0.002 ± 0.002</td>
<td>0.01 ± 0.17</td>
</tr>
<tr>
<td>1.0 at.%, 800 °C</td>
<td>3.3 ± 0.2</td>
<td>0.014 ± 0.003</td>
<td>1.67 ± 0.22</td>
</tr>
<tr>
<td>1.0 at.%, 1100 °C</td>
<td>12.7 ± 0.5</td>
<td>-0.002 ± 0.003</td>
<td>0.37 ± 0.27</td>
</tr>
<tr>
<td>3.6 at.%, 650 °C</td>
<td>2.5 ± 0.3</td>
<td>0.019 ± 0.006</td>
<td>2.6 ± 0.7</td>
</tr>
</tbody>
</table>
length contraction and (b) the increase in Debye-Waller factor compared to the bulk standard as a function of inverse nanoparticle diameter. As indicated by the line of best fit, we observe a linear trend in both cases. From Figure 5.12(b) this suggests that the increased disorder in the nanoparticles is predominantly located at the surface as discussed above.

The bond length contraction, $\delta R$, can be related to the surface tension, $\gamma$, through a simple liquid-drop model [24]:

$$\delta R = \frac{4}{3} \cdot \frac{1}{D} \cdot K R_b \gamma$$

(5.2)

where $K$ is the bulk compressibility, $R_b$ is the bulk bond length and $D$ is the nanoparticle diameter. Using a bulk Cu compressibility of $7.1 \times 10^{-3}$ GPa$^{-1}$ [19] and the bulk Cu bond length given in Table 5.6, a surface tension of $2.5 \pm 0.4$ J/m$^2$ can be estimated. This value exceeds that of the surface tension simulated for free-standing Cu nanoparticles [32], which indicates the significant influence of the matrix. Similar results were found for Au [106] and Pt nanoparticles [107], formed by ion beam synthesis in amorphous SiO$_2$.

5.3.6 Thermal characteristics

The 8.6 and 1.0 at.% samples, both annealed at 800 °C, where measured as a function of measurement temperature (15K to 295K) and compared to the bulk Cu standard. These two samples contained nanoparticles of average diameter 14.0 and 3.3 nm, respectively (Table 5.6). Neither sample contained a measurable amount of Cu-O bonding, with the coordination number being 12.1 $\pm$ 0.3 and 10.6 $\pm$ 0.5 atoms, respectively (Table 5.4). The temperature dependent EXAFS data was analyzed following two different methods: individual fits and multiple fits. The former is the standard method followed in the previous sections, while
5.3. RESULTS AND DISCUSSION

Figure 5.12: Combined analysis of EXAFS and SAXS results: (a) relative bond length contraction and (b) increase in Debye-Waller factor of the nanoparticles (as compared to the bulk Cu standard) as a function of inverse nanoparticle diameter.
the multiple fit method is explained below. For both methods the amplitude reduction factor ($S_0^2$) and the shift in the threshold energy for the removal of a core electron ($E_0$) were determined from the bulk Cu standard and fixed to these values for the nanoparticle analysis as per usual. Given the increased disorder with increasing temperature, the structural parameters were determined using a $k^2$-weighting and $k$ and $r$ ranges of 3.5 - 11 Å$^{-1}$ and 1.64 - 2.84 Å, respectively.

For the multiple fit method all temperatures for each sample were fitted simultaneously. In order to reduce the number of fitting parameters and break the correlation between the bond length and the third cumulant ($C_3$), the temperature ($T$) dependence of the Debye-Waller factor ($\sigma^2$) and $C_3$ were restrained by [108]:

$$\sigma^2(T) = \frac{\hbar \omega_E}{2k_e} \frac{1 + z}{1 - z} + \sigma^2_{\text{static}}$$

and:

$$C_3(T) = \frac{k_3(\hbar \omega_E)^2}{2k_e^3} \frac{1 + 10z + z^2}{(1 - z)^2} + C_{3,\text{static}}$$

where $\sigma^2_{\text{static}}$ and $C_{3,\text{static}}$ are the static (temperature independent) contributions to the total disorder and assymmetry, respectively. $k_e$ and $k_3$ are the effective harmonic spring constant and cubic anharmonicity constant, respectively, of the anharmonic effective pair potential [108]. The former constant is given by $k_e = \mu \omega_E^2$. Here, $\mu$ is the reduced mass (in this case for a Cu-Cu pair) and $\omega_E$ is the Einstein frequency, an atomistic measure of lattice stiffness.$^1$ The Einstein temperature is given by $\Theta_E = \hbar \omega_E / k_B$, where $k_B$ is the Boltzman constant. The $z$ in Equations 5.3 and 5.4 is defined as $z = \exp(-\Theta_E / T)$. Relative to a standard, a more rapidly increasing temperature dependent Debye-Waller factor indicates a less stiff bonding environment with a lower $\Theta_E$. The opposite is true for a slowly increasing Debye-Waller factor (stiffer bonds, greater $\Theta_E$).

$^1$ $\omega_E$ is the mean value of the phonon frequency $\nu$ introduced in Chapter 1.
5.3. RESULTS AND DISCUSSION

Figure 5.13(a) shows the FTs of the bulk standard as a function of the measurement temperature, while Figure 5.13(b) shows the FTs of the bulk and nanoparticle samples at a fixed measurement temperature of 100K. From Figure 5.13(a) we observe a decrease in the first nearest neighbor peak amplitude with increasing measurement temperature, as illustrated graphically in the inset. Given that the coordination number is not dependent upon the measurement temperature, these observations are consistent with the expected increase in thermal disorder upon heating from 15K. In Figure 5.13(b) we see, as expected, a broader peak of lesser amplitude for the small nanoparticle sample as compared with the bulk standard and the large nanoparticle sample. The latter two FTs are comparable. These qualitative results are consistent with those presented previously for the 15K measurements.

Figure 5.14(a) shows the evolution of the Debye-Waller factor with measurement temperature for all samples. The dotted lines represent the multiple fits, while the individual points represent the individually fitted spectra. Qualitatively, we can observe (from the multiple fits) that the smaller nanoparticles have a smaller $\Theta_E$, given the greater slope at the high temperature end. Meanwhile, $\Theta_E$ for the larger nanoparticles appears to be comparable to that for the bulk standard. However, the individually fitted spectra may tell a different story. For example, in Figure 5.14(b) the individual data points for the 3.3 nm nanoparticle sample are shown. Equation 5.3 has been applied to extract $\Theta_E$. To illustrate the limitations of the temperature dependent EXAFS analysis, the following fits were made. First, all measurement points including 295K where fitted (black line). Then, by increasing the Debye-Waller factor at 295K to its “maximum” value (measured value plus EXAFS fitting error), the data were fitted again (blue line). This value for the Debye-Waller factor is indicated by the blue arrow. Sim-
Figure 5.13: Fourier Transforms of $k^2$-weighted EXAFS spectra: (a) the bulk sample as a function of measurement temperature with the peak amplitude inset and (b) bulk and nanoparticle samples at a fixed measurement temperature of 100K.
Figure 5.14: Temperature dependent Debye-Waller factors as extracted by individual and multiple fitting procedures. In (a) the dotted lines represent the multiple fits, while the individual points are extracted from the individually fitted spectra. The measurement uncertainty is graphically represented in (b), where the individual measurement points are fitted to the Einstein model (Equation 5.3). Further details are given in the text.
ilarly, by decreasing the Debye-Waller factor at 295K to its “minimum” value (measured value minus error), the data were fitted with the red line. This value for the Debye-Waller factor is indicated by the red arrow. Finally, excluding the 295K Debye-Waller factor altogether gives the green line. Table 5.7 summarizes the results when following the steps described above for each sample. Here, the multiple fits are also included.

In general, we observe that \( \Theta_E \) depends critically on the value for the Debye-Waller factor at high measurement temperatures. For the bulk standard it is reassuring to note that a fit up to 295K gives a very similar \( \Theta_E \) as a fit up to 220K (equal to within 1.6%) both for the individual as well as the multiple fit approach. The extracted value for \( \Theta_E \) of the bulk standard also agrees with a previously published value of \( (238.0 \pm 2.4)K \) as extracted by temperature dependent EXAFS analysis of a 5 \( \mu \)m Cu foil [109]. For the nanoparticle samples, comparing the individual fits up to 295K and 220K, respectively, we find relatively large discrepancies of about 6 - 8% in \( \Theta_E \). This is consistent with Figure 5.14(a) where the 295K measurement point for both nanoparticle samples appears off trend. For the remainder of the discussion this measurement temperature will be omitted, for the nanoparticle samples, and the results of the multiple fit approach will be presented.

With the above justification in mind, \( \Theta_E \) for the nanoparticle samples are \( (233.5 \pm 5.5)K \) and \( (217.3 \pm 9.5)K \) for the 14.0 and 3.3 nm samples, respectively. Comparing this to the bulk value of \( (235.4 \pm 4.7)K \), the decrease in \( \Theta_E \) for the smallest nanoparticle size signifies an overall loosening of the Cu-Cu bonds where the thermal disorder increases more rapidly with increasing temperature. Two factors influence the thermal disorder of nanoparticles [32]. First, nanoparticle surface curvature causes a capillary pressure on the core, which results in stiffer
Table 5.7: Einstein temperatures determined by fitting the individually measured Debye-Waller factors of the bulk Cu standard, 14.0 nm (8.6 at.%, 800 °C) and 3.3 nm (1.0 at.%, 800 °C) nanoparticle samples as compared with a multiple fit analysis approach.

<table>
<thead>
<tr>
<th>Bulk standard:</th>
<th>Einstein temperature, $\theta_E$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Individual fits</td>
</tr>
<tr>
<td>To 295K, mean ($\theta_E^{295K}$)</td>
<td>236.4 ± 2.8</td>
</tr>
<tr>
<td>To 295K, upper range</td>
<td>240.7 ± 4.3</td>
</tr>
<tr>
<td>To 295K, lower range</td>
<td>231.9 ± 2.2</td>
</tr>
<tr>
<td>To 220K, mean ($\theta_E^{220K}$)</td>
<td>232.7 ± 4.0</td>
</tr>
<tr>
<td>Difference, $\theta_E^{220K}/\theta_E^{295K}$</td>
<td>1.6 %</td>
</tr>
</tbody>
</table>

14.0 nm nanoparticles:

|                       | Individual fits | Multiple fit |
| To 295K, mean ($\theta_E^{295K}$) | 213.3 ± 7.0 | 226.2 ± 5.7 |
| To 295K, upper range   | 224.6 ± 3.4 | -           |
| To 295K, lower range   | 203.8 ± 9.8 | -           |
| To 220K, mean ($\theta_E^{220K}$) | 231.2 ± 3.6 | 233.5 ± 5.5 |
| Difference, $\theta_E^{220K}/\theta_E^{295K}$ | 8.4 % | 3.2 % |

3.3 nm nanoparticles:

|                       | Individual fits | Multiple fit |
| To 295K, mean ($\theta_E^{295K}$) | 194.0 ± 6.0 | 213.6 ± 8.0 |
| To 295K, upper range   | 204.2 ± 4.6 | -           |
| To 295K, lower range   | 185.4 ± 8.2 | -           |
| To 220K, mean ($\theta_E^{220K}$) | 205.4 ± 8.3 | 217.3 ± 9.5 |
| Difference, $\theta_E^{220K}/\theta_E^{295K}$ | 5.9 % | 1.7 % |
bonds ($\Theta_E$ increases). Second, the increased fraction of under-coordinated surface atoms with higher disorder causes a greater fraction of looser bonds ($\Theta_E$ decreases). These two factors are competing, and it is not intuitive that one factor will dominate the other as the nanoparticle size decreases. However, the results presented here, clearly suggest that with decreasing nanoparticle size, the surface term (looser bonds) dominates and causes a decrease in $\Theta_E$ of $\sim 8\%$ for the smallest nanoparticle size. This is similar to embedded Ag nanoparticles of 2.8 nm average diameter, which were reported with a $\sim 6\%$ decrease in $\Theta_E$ as compared to a bulk Ag standard [110]. This value was, however, potentially influenced by the presence of an O-rich Ag environment, and no error analysis was reported. Similar reports on Cu nanoparticles are not available.

Figure 5.15 shows the evolution of the bond length and third cumulant as a function of measurement temperature. Although the temperature-dependent bond length evolution for the 14.0 nm nanoparticle sample is comparable to that for the bulk, differences in the third cumulant shows that a distorted structural environment is still present consistent with a greater Debye-Waller factor. For the 3.3 nanoparticle sample, both the bond length and (particularly) the third cumulant increases faster than is the case for the bulk standard. This indicates a larger thermal expansion coefficient present for the small nanoparticles, where the bond length distribution is significantly asymmetric.

5.4 Summary

In summary, this chapter has investigated the concentration- and annealing-temperature-dependent structure of Cu nanoparticles formed in amorphous SiO$_2$ by ion beam synthesis. In general, Cu is a sufficiently fast diffuser in SiO$_2$ to
Figure 5.15: Measurement temperature dependent structural parameters for a bulk Cu standard and 14.0 and 3.3 nm nanoparticle samples: (a) bond length and (b) third cumulant. Data were extracted using the multiple fit approach.
facilitate nanoparticle formation during annealing. The nanoparticles were of spherical shape and single crystalline, retaining the bulk fcc phase. For a sufficiently high Cu concentration (8.6 at.% Cu) nanoparticles were formed in the as-implanted state, while for the lowest concentration (0.3 at.% Cu) a loss of material was observed after annealing at high temperatures (800 and 1100 °C).

Cu was found in an oxidized state at low annealing temperatures and low concentrations. In such environment, XANES spectra indicated that Cu prefers a square coordination of O atoms in the first shell (as in Cu₂O). Nanoparticles were in general found to exhibit a suppressed coordination number, due to the increased fraction of surface atoms, together with a decreased bond length, increased structural disorder, and a negative third cumulant. This is attributed to atoms at the nanoparticle surface being under-coordinated and with a reconstructed or distorted configuration.

All structural parameters were both concentration- and annealing-temperature-dependent. Increasing concentration and annealing temperature resulted in a decrease in structural disorder (both Gaussian and non-Gaussian), with increasing coordination number and bond length. Samples annealed at 1100 °C retained structural parameters consistent with those of the bulk Cu standard (except 0.3 at.% due to Cu evaporation).

Size distributions determined by SAXS analysis combined with structural parameters determined by EXAFS analysis indicated a linear relationship between an increased bond length contraction and increased Debye-Waller factor as a function of inverse nanoparticle diameter. The latter suggests that the increased disorder (compared with the Cu standard) is predominantly located at the surface. From the size dependent bond length contraction, the nanoparticle surface tension was estimated to 2.5 ± 0.4 J/m², exceeding the surface tension simulated
for free-standing Cu nanoparticles. This indicates the host matrix influences the surface structure of embedded nanoparticles.

Temperature dependent EXAFS measurements revealed that for small nanoparticles (3.3 nm average), the thermal component of the disorder increased faster than for larger nanoparticles (14.0 nm average) and the bulk standard. This implies that on average the Cu-Cu bonds are looser in the 3.3 nm nanoparticles consistent with the large fraction of reconstructed surface atoms. The thermal characteristics of the 14.0 nm nanoparticles were comparable to that of the bulk standard, although for the nanoparticles the third cumulant increased faster with increasing measurement temperature.

The following chapter presents the results and discussions on ion beam synthesized Zn nanoparticles.
Chapter 6

Formation of Zn Nanoparticles

This chapter discusses the formation of Zn nanoparticles in smartphone EIG, as a function of synthesis parameters, including the preparation In concentration and thermal annealing temperature. For the parameters used with respect to the nanoparticles size, single hexagonal-structured Zn nanocrystals were synthesized in the undoped Zn concentration. However, in order to form In nanocrystals only (and In-Zn bonds only), the annealing temperature needed to be relatively high. In fact, this occurred only at 400°C, while at lower temperatures, Zn nanocrystals of different fractions of Zn atoms and bonds to In (detected by XRD). On the other hand, annealing at 400°C meant the In contribution to be very weak, consisting of a large number of small nanoparticles for In and only a few large nanoparticles up to 25 nm. Given the large number of small nanocrystals, the volume-weighted average nanoparticle size at this annealing temperature was 4-5 nm. The long-range atomic structure, as measured by XRD, was hexagonally close-packed as for the bulk standard. The short-range atomic structure size measured by HRTEM to be different from that of the bulk In plane.
Chapter 6

Formation of Zn Nanoparticles

This chapter discusses the formation of Zn nanoparticles in amorphous SiO₂ as a function of synthesis parameters, including the implanted Zn concentration and thermal annealing temperature. For the parameters used here, neither the nanoparticle size, size distribution or atomic structure was dependent on the implanted Zn concentration. However, in order to form Zn nanoparticles only (that is Zn-Zn bonds only), the annealing temperature needed to be relatively high. In fact, this occurred only at 800°C, while at lower temperatures there was a significant fraction of Zn atoms not bonding to Zn (dissolved in the matrix). On the other hand, annealing at 800°C caused the size distribution to be very broad, consisting of a large number of small nanoparticles (~3 nm) and a few large nanoparticles (up to 25 nm). Given the large number of small nanoparticles the volume-weighted average nanoparticle size at this annealing temperature was 4 - 5 nm. The long-range atomic structure, as measured by WAXS, was hexagonally close packed as for the bulk standard. The short-range atomic structure was measured by EXAFS to be different from that of the bulk Zn phase.
6.1 Introduction

Zn ion implantation is commonly used to form ZnO nanoparticles [111]. ZnO is a wide band gap semiconductor material [112] for which its large exciton binding energy allows excitonic recombination and optically pumped laser oscillations at room temperature [113]. Commonly, ZnO nanoparticles are formed by subsequent implantation of Zn and O ions [112] or Zn ion implantation followed by annealing in an oxidizing atmosphere [114, 115, 116]. By annealing samples implanted with only Zn ions in a reducing atmosphere, mono-elemental Zn nanoparticles are formed, for example in SiO$_2$ [116] or MgO [117] matrices. Metallic Zn nanoparticles are interesting due to their optical properties (surface plasmon resonance) [117] that depend on the nanoparticle size. However, literature on the short-range atomic structure of Zn nanoparticles is sparse.

The present study seeks to investigate the atomic structure of Zn nanoparticles synthesized in SiO$_2$ by ion implantation and thermal annealing and compare this to the bulk structure. Zn in its bulk form is a hexagonally close packed (hcp) structure. The hcp structure is similar to that of fcc, however the first shell is split into two. Each of these contains six atoms and are separated by $\sim 0.25$ Å. As far as the author is aware, there has been no reports on the short-range atomic structure in Zn nanoparticles.

6.2 Experimental

Nanoparticle formation

0.6 μm SiO$_2$ films, grown on Si(100) substrates by wet thermal oxidation, were implanted with 450 keV $^{64}$Zn ions at room temperature. Two different fluences
(5x10^{16} \text{ and } 1\times10^{17} \text{ cm}^{-2}) \text{ resulted in two different peak Zn concentration of } 3.2 \text{ and } 6.4 \text{ at.\%}, \text{ respectively. The samples were then annealed in a reducing atmosphere (5\% H}_2 \text{ in N}_2) \text{ for 1 h at temperatures up to 800 °C.}

**Nanoparticle characterization**

The nanoparticles were characterised utilizing RBS, TEM, WAXS and EXAFS and the atomic structure was then compared with that of the bulk sample. The latter was formed by evaporating 300 nm of Zn onto a SiO$_2$ substrate. Additionally, a bulk ZnO standard was prepared from ZnO powder.

RBS was performed using 2.0 MeV He$^{2+}$ ions. This enabled investigation of the Zn implantation profile to a depth of $\sim 0.6 \mu\text{m}$. Cross-sectional TEM analysis was performed to enable quantitative examination of the nanoparticle shape as well as size and depth distributions. WAXS measurements were performed in transmission mode to investigate the nanoparticle crystallographic phase as compared with the bulk standard. The WAXS samples were the same as those used for EXAFS to ensure consistency and were measured at room temperature using 0.517 Å x-rays at normal incidence and a minimum sample-to-detector distance of 123 mm.

EXAFS spectroscopy was utilized to determine the short-range atomic structure of the nanoparticles as compared with the bulk Zn standard. Measurements were performed in fluorescence mode at the Zn K-edge (9.659 keV) up to $k = 16$ Å$^{-1}$. All samples were measured at a minimum achievable temperature of 16K (liquid He sample environment) to minimise thermal disorder. EXAFS samples were prepared using the standard technique as illustrated in Figure 3.15.
6.3 Results and discussion

6.3.1 RBS

Figure 6.1 shows the Zn concentration profiles measured by RBS as a function of SiO₂ depth. We note that the profiles are comparable for both the 3.2 and 6.4 at.% samples at all annealing temperatures. Up to 600 °C the Zn profiles are near Gaussian, while at 800 °C they are markedly non-Gaussian. The latter indicates significant thermal diffusion where the concentration profile has narrowed. Moreover, Zn atoms have migrated both towards the surface and towards the underlaying Si substrate. However, the total amount of Zn in each sample was constant upon annealing at higher temperatures.

6.3.2 TEM and WAXS

Figure 6.2 shows cross-sectional TEM images for both samples annealed at 600 and 800 °C (at 400 °C no nanoparticles were observed). The nanoparticles were spherical and single crystalline for both concentrations and annealing temperatures. For the samples annealed at 600 °C, only small nanoparticles were found as shown at a higher magnification in Figures 6.2(a) and (b). On the other hand, we observe that for the 800 °C anneals the nanoparticle size varies significantly with depth. In the shallow region, closest to the SiO₂ surface, there are a large number of small nanoparticles ~ 3 nm in diameter for both concentrations (not shown). Meanwhile, in the deep region closest to the Si substrate there are a number of large nanoparticles (up to 25 nm in diameter) as can be seen in Figure 6.2(c) and (d). The reason for this broad size distribution is potentially a strongly defect-mediated nucleation process [118], where the large nanoparticles are formed in the region where there are few structural defects in the matrix (that is the end
Figure 6.1: RBS spectra for the 3.2 and 6.4 at.% Zn samples.
Table 6.1: Estimates of average nanoparticle diameters based on TEM analysis.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Zn concentration 3.2 at.%</th>
<th>Zn concentration 6.4 at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 °C</td>
<td>3.0 ± 1.0 nm</td>
<td>3.2 ± 1.0 nm</td>
</tr>
<tr>
<td>800 °C</td>
<td>4.8 ± 1.0 nm</td>
<td>4.2 ± 1.0 nm</td>
</tr>
</tbody>
</table>

of the implanted range). An alternative explanation lies in the thickness of the matrix. It has been observed previously that for Ge implanted into SiO$_2$ followed by thermal annealing, Ge atoms diffuse away from the implanted region (towards the interface) when the SiO$_2$ layer thickness is less than $\sim 0.5$ μm [119, 120]. This tendency has not been observed for 2.0 μm SiO$_2$ implants [53]. The nanoparticle size distributions, shown in Figure 6.3, were determined from micrographs covering the extent of the implanted depth range. The volume-weighted average diameters are listed in Table 6.1 and show that neither the concentration or annealing temperature appreciably influence the average nanoparticle size. However, as seen above, the annealing temperature does influence the nanoparticle size distribution.

Figure 6.4(a) shows the WAXS profiles for the 800 °C samples as compared with the bulk standard$^1$. Inset are the three most prominent diffraction peaks of hcp Zn. The measured peaks of the nanoparticle samples, shown in Figure 6.4(b), are in excellent agreement with those for the bulk standard and those expected for a hcp Zn structure as opposed to fcc. Zn oxides were not observed

$^1$For the samples annealed at 600 °C diffraction peaks were less prominent given the presence of only small nanoparticles. However, the phase was established to be hcp from electron diffraction (not shown).
Figure 6.2: TEM micrographs of Zn nanoparticles in SiO₂. In (a) and (b) the 3.2 and 6.4 at.% samples, respectively, annealed at 600 °C are shown at high magnification. In (c) and (d) the same samples annealed at 800 °C are shown (at lower magnification). In (c) and (d) the deep region (towards the Si substrate) contains large nanoparticles and the shallow region (opposite direction) contains small nanoparticles (not resolved at this magnification).
Figure 6.3: Nanoparticle size distributions corresponding to the TEM images in Figure 6.2.
by analyzing the WAXS spectra (not shown).

6.3.3 EXAFS

Figure 6.5(a) shows $k^2$-weighted EXAFS spectra measured for different annealing temperatures comparing the 6.4 at.% Zn samples with the bulk Zn standard. The trend for the 3.2 at.% samples was qualitatively similar to that of the higher concentration. For the bulk standard we note that the first nearest neighbor is split in two, consistent with the hcp phase. Each shell contains six atoms in its bulk phase, located at phase-corrected radial distances of $\sim 2.6$ and $2.9 \text{ Å}$. For the implanted samples there is a significant contribution of scattering between the absorber and first nearest Zn neighbor shell present at annealing temperatures of 400 and $600 \degree C$ (for the former no nanoparticles were observed by TEM). The presence of low-$r$ scattering indicates that Zn atoms are dissolved in the matrix and bonding to constituent atoms. The inset in Figure 6.5(a) shows the bulk ZnO spectrum compared with the two lowest annealing temperatures, confirming the presence of Zn-O bonds in the latter samples. For example, for the $600 \degree C$ sample there is a co-existence of both Zn-Zn and Zn-O bonds. Note that the presence of Zn-O bonds do not imply the existence of ZnO nanoparticles given the absence of a the second shell located at $\sim 3.1 \text{ Å}$ (consistent with WAXS measurements).

The Zn-Zn bonding environment was fitted for the $800 \degree C$ samples and the bulk standard, as shown in Figure 6.5(b)\(^2\). The results are summarized in Table 6.2 and graphically presented in Figure 6.6. We note that the first shell coordination number for the nanoparticle samples is comparable to the bulk value, while the

\(^2\)For the lower annealing temperatures fits were not performed given the significant fraction of Zn-O bonds. With an appropriate Zn silicate standard, XANES analysis could be utilized to quantify the fraction of Zn-O bonds [92].
Figure 6.4: WAXS measurements of the 800 °C samples and bulk standard. In (a) the WAXS profiles are shown with the three most prominent diffraction peaks inset. In (b) the measured diffraction peaks of each sample are compared with those of bulk hcp and fcc Zn.
second shell value is significantly lower than that of the bulk. Concurrently, the Debye-Waller factor is smaller in the second shell as compared with the first shell. There is no physical explanation for this, in fact the Debye-Waller factor should increase further away from the absorber [121]. Considering a structural parameter correlation between the coordination number and Debye-Waller factor we note the following. If the estimated coordination number (from EXAFS analysis) is smaller than the real coordination number, this will be compensated by a greater (estimated) Debye-Waller factor. The most probable reason this occurs here, is that the shells are close enough to significantly overlap, but not close enough to be treated as one single shell in the EXAFS fitting procedure. More obvious correlation issues were encountered when the third cumulant was included in the fit (not shown). The third cumulant is strongly correlated with the bond length, and thus the fitting results are inconclusive.

6.4 Conclusions

In summary, this chapter has investigated ion beam synthesized Zn nanoparticles embedded in amorphous SiO₂. For the given Zn concentrations (6.4 and 3.2 at.%) an annealing temperature of 600 °C was required to form hcp nanoparticles. However, at this annealing temperature, there was still a significant fraction of Zn atoms dissolved in the matrix as observed by EXAFS. At 800 °C on the other hand there was predominantly a Zn-Zn bond environment implying the majority of Zn atoms had formed nanoparticles. At this temperature the nanoparticles were also of the hcp phase and with an average diameter of 4 - 5 nm (depending on implanted Zn concentration). In general, the Zn concentration had little effect on the either the nanoparticle size, size distribution or the measured short-range
Figure 6.5: Fourier-transformed EXAFS spectra. In (a) as a function of phase-corrected radial distance comparing the different annealing temperatures of the 6.4 at.% samples with the bulk Zn standard and (inset) compared with the bulk ZnO standard. In the inset, the scattering between the first (O) and second (Zn) shell in ZnO, stems from the first scattering shell in Zn metal. In (b) the fits to the bulk Zn standard and both 800 °C anneals are shown (non-phase-corrected).
Table 6.2: Structural parameters of bulk Zn and Zn nanoparticles (annealed at 800 °C) as extracted by $k^2$-weighted EXAFS analysis. Legend: CN = coordination number, BL = bond length, DW = Debye-Waller factor.

<table>
<thead>
<tr>
<th></th>
<th>CN</th>
<th>BL</th>
<th>DW</th>
</tr>
</thead>
<tbody>
<tr>
<td>(atoms)</td>
<td>(Å)</td>
<td>$(10^{-3}$ Å²)</td>
<td></td>
</tr>
<tr>
<td><strong>First shell:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk standard</td>
<td>6 (fixed)</td>
<td>2.655 ± .002</td>
<td>4.9 ± .2</td>
</tr>
<tr>
<td>6.4 at.%</td>
<td>6.4 ± .9</td>
<td>2.666 ± .005</td>
<td>5.8 ± .8</td>
</tr>
<tr>
<td>3.2 at.%</td>
<td>5.8 ± .9</td>
<td>2.665 ± .007</td>
<td>5.1 ± 1.0</td>
</tr>
<tr>
<td><strong>Second shell:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk standard</td>
<td>6 (fixed)</td>
<td>2.875 ± .002</td>
<td>3.6 ± .2</td>
</tr>
<tr>
<td>6.4 at.%</td>
<td>3.5 ± .8</td>
<td>2.885 ± .006</td>
<td>4.1 ± 1.1</td>
</tr>
<tr>
<td>3.2 at.%</td>
<td>4.6 ± 1.1</td>
<td>2.883 ± .008</td>
<td>6.0 ± 1.9</td>
</tr>
</tbody>
</table>
Figure 6.6: Extracted structural parameters of Zn nanoparticle samples (annealed at 800 °C) as compared to the bulk Zn standard: (a) coordination number, (b) bond length, (c) Debye-Waller factor. The dotted lines represent the bulk values.
atomic structure. For the latter, at $800^\circ$C, the nanoparticles had a reduced second shell coordination number while the first shell retained the bulk coordination number. Concurrently, the Debye-Waller factor of the second shell was smaller than that of the first (both for the bulk and nanoparticle samples). This indicated parameter correlation between the coordination number and Debye-Waller factor that was not overcome. Further investigation into formation of Zn nanoparticles was not performed.

The following chapter will discuss the ion irradiation of embedded Cu nanoparticles and how this affects the short-range atomic structure.
Chapter 7

Ion Irradiation of Cu Nanoparticles

This chapter discusses the ion-irradiation-induced structural changes of ion-irradiated Cu nanoparticles. Ion irradiations were performed at high temperature and under various conditions. The structural changes were quantified and found to depend on the irradiation conditions, resulting in significant changes in the crystalline structure. However, at intermediate ion doses, the Cu nanoparticles exhibited a short-range cluster structure, comparable to that reported for an amorphous metallic state. Moreover, temperature-dependent XAS measurements revealed that the thermal characteristics of the amorphous nanoparticles were significantly different from those in an irradiated state.
Chapter 7

Ion Irradiation of Cu Nanoparticles

This chapter discusses the ion-irradiation-induced structural changes of embedded Cu nanoparticles. Ion irradiations were performed at both liquid $N_2$ and room temperatures. For both temperatures the fraction of Cu dissolved in the matrix was quantified and found to increase with increasing nuclear stopping (expressed as displacements per atom - dpa) eventually yielding complete dissolution of the nanoparticles. However, at intermediate dpa values the Cu nanoparticles exhibited a short-range atomic structure comparable to that expected for an amorphous elemental metal. Moreover, temperature dependent EXAFS measurements revealed that the thermal characteristics of the amorphous nanoparticles were significantly different from those in an unirradiated state.
CHAPTER 7. ION IRRADIATION OF CU NANOPARTICLES

7.1 Introduction

Amorphous metals are commonly alloys comprised of at least two different atomic species in order to stabilize the amorphous structure. The recrystallization rate of pure elemental amorphous metals is generally too great to quench in the amorphous phase [48]. The production of elemental amorphous metals requires an extremely rapid cooling rate of the order of $10^9$ Ks$^{-1}$ from the melt [122]. This is possible with a sonochemical process as demonstrated for amorphous Fe [122], Ni [123] and Cu [124]. The latter two reports do not provide information on the short-range atomic structure, whereas the former reports a first shell coordination number of $\sim 10$ atoms.

Ion irradiation was once considered a promising tool for amorphization of bulk elemental metals given the highly non-equilibrium nature of the ion stopping process in matter. However, as discussed in Chapter 1, the extent of disorder in irradiated bulk elemental metallic structures saturates prior to amorphization [48]. Given the results for ion irradiation of elemental semiconductors, where Ge nanoparticles were rendered amorphous at a fluence approximately two orders of magnitude below that required for bulk Ge [52], the present chapter will explore the ion-irradiation-induced structural changes in embedded Cu nanoparticles.

7.2 Experimental

7.2.1 Nanoparticle formation

2 $\mu$m SiO$_2$ films, grown on Si(100) substrates by wet thermal oxidation, were implanted with $^{63}$Cu ions. A multiple energy (0.7, 0.9, 1.2, 1.5 MeV), multiple fluence (2.1, 4.2, 5.2, 7.2x$10^{16}$ cm$^{-2}$) implant sequence yielded a near-constant
Cu concentration of 3.6 at.% over a depth range of approximately 0.6 - 1.0 μm [16]. To minimise diffusion, implantations were performed at liquid N\textsubscript{2} temperature (LNT) and fluxes were maintained at power levels < 0.7 W cm\textsuperscript{-2}. Following implantation, the supersaturated samples were annealed in flowing forming gas (5\% H\textsubscript{2} + 95\% N\textsubscript{2}) for one hour at a temperature of 650 °C to induce precipitation and nanoparticle growth. The choice of Cu concentration and annealing temperature was based on the results in Chapter 5 with the aim of producing Cu nanoparticles only and suppressing the formation of Cu-O bonds. A bulk Cu standard was prepared by depositing 220 nm of Cu on SiO\textsubscript{2} by thermal evaporation. The Cu layer was polycrystalline and approximately ten times the effective thickness of the implanted Cu ions. To achieve a comparable thickness of SiO\textsubscript{2} overlayer for both the nanoparticle and polycrystalline samples, 0.6 μm of SiO\textsubscript{2} was then deposited on top of the Cu layer by plasma enhanced chemical vapour deposition.

### 7.2.2 Nanoparticle irradiation

Two studies were undertaken. In the first study the Cu nanoparticles and bulk Cu standard were irradiated simultaneously with 5.0 MeV \textsuperscript{120}Sn ions in the fluence range \(10^{13} - 10^{16}\) cm\textsuperscript{-2} at LNT. The ion energy was chosen to yield a projected range beyond the SiO\textsubscript{2} film (i.e. within the Si substrate) to negate impurity effects due to Sn. The ion energy loss due to nuclear and electronic stopping at 0.6 μm was, respectively, ~ 0.8 and 1.4 keV/nm in SiO\textsubscript{2} and ~ 2.4 and 2.3 keV/nm in Cu as simulated by TRIM [16]. For a fluence of 1x10\textsuperscript{14} cm\textsuperscript{-2}, for example, the latter is equivalent to 0.16 displacements per atom (dpa).

In the second study the nanoparticles were irradiated at room temperature (RT) with either \textsuperscript{120}Sn or \textsuperscript{74}Ge ions at a variety of energies (all sufficient to
yield a projected range beyond the SiO₂ film). The ion species and energy combination was varied such that each irradiation imposed a different ratio of nuclear/electronic energy loss to the embedded nanoparticles. The irradiation conditions are presented in Table 7.1.

Table 7.1: Parameters for room temperature ion irradiation of Cu nanoparticles embedded in 2.0 μm SiO₂. The last column gives the nuclear/electronic energy loss ratio.

<table>
<thead>
<tr>
<th>Species</th>
<th>Energy (MeV)</th>
<th>Fluence (10^{14} cm^{-2})</th>
<th>Cu dpa</th>
<th>S_{n}/S_{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>5.0</td>
<td>1.0</td>
<td>0.16</td>
<td>1.04</td>
</tr>
<tr>
<td>Sn</td>
<td>6.0</td>
<td>1.2</td>
<td>0.18</td>
<td>0.82</td>
</tr>
<tr>
<td>Ge</td>
<td>3.5</td>
<td>2.4</td>
<td>0.20</td>
<td>0.71</td>
</tr>
<tr>
<td>Ge</td>
<td>6.0</td>
<td>3.7</td>
<td>0.24</td>
<td>0.27</td>
</tr>
</tbody>
</table>

7.2.3 Nanoparticle characterization

The Cu distribution in the SiO₂ samples was probed by RBS. The depth distribution of implanted Cu was consistent with TRIM simulations (not shown) and remained virtually unchanged upon annealing or irradiation. Cross-sectional TEM samples were prepared using standard techniques at low temperatures to inhibit diffusion and/or recrystallization during preparation. For example, glue curable at room temperature under UV light was utilized and Ar ion milling was performed at LNT. TEM analysis was carried out at 300 keV and exposure to the electron beam was minimized. The nanoparticle shape, size and crystallinity
were investigated. The nanoparticle size distribution was also determined with transmission SAXS measurements using 1.5 Å x-rays. To eliminate parasitic scattering, the substrate was removed prior to exposure (as described below). The volume-weighted size distribution and volume-weighted average diameters were calculated.

EXAFS spectroscopy was utilized to determine the bond length, coordination number, Debye-Waller factor and the third cumulant of the interatomic distance distribution of the first nearest neighbor shell. Measurements were performed in fluorescence mode at the Cu K-edge (8.979 keV). All samples were measured at a minimum achievable temperature of 12K (liquid He sample environment) to minimise thermal disorder. Selected samples were also measured at elevated temperatures (up to room temperature) to investigate thermal characteristics. EXAFS samples were prepared using the standard technique as illustrated in Figure 3.15. Fluorescence spectra were recorded for both nanoparticle samples and the reference compounds. The latter comprised of bulk polycrystalline Cu with grain size ∼ 220 nm and bulk Cu₂O powder. The Cu areal density of both standards was comparable to that of the Cu nanoparticle samples. For both standards and nanoparticle samples, the Cu K-edge fluorescence signal comprised 50 - 70 % of the incoming count rate, the latter maintained within the linear counting regime of the detector. Fluorescence spectra were recorded to $k = 18$ Å⁻¹ at 12K, while 15 Å⁻¹ sufficed for the temperature dependent study given the increase in thermal disorder.
7.3 Results and discussion

In this section the results of the LNT and RT irradiations are presented. For the former we will argue, in particular, for the existence of an amorphous Cu phase after ion irradiation of the nanoparticles with a fluence of $1 \times 10^{14}$ cm$^{-2}$ $^{120}$Sn ions (hereafter units will be omitted for simplicity). Finally, thermal characteristics of unirradiated and irradiated nanoparticles, as compared to the bulk Cu standard, will be presented.

7.3.1 LNT irradiation: nanoparticle shape and size

Figure 7.1 shows a range of TEM micrographs, including (a) unirradiated and (b)-(e) irradiated nanoparticles (successive irradiation fluences of $6 \times 10^{13}$, $1 \times 10^{14}$, $3 \times 10^{14}$ and $1 \times 10^{15}$). The nanoparticles are of spherical shape both before and after irradiation (apart from the highest fluence). Prior to irradiation, the nanoparticles exhibit the fcc structure, as measured by electron diffraction (not shown) and are randomly oriented within the amorphous SiO$_2$. In the inset of Figure 7.1(a), the (111) lattice planes of fcc Cu are discernible in the high-resolution image. Upon irradiation at $1 \times 10^{14}$, lattice fringes could not be resolved.

For the unirradiated nanoparticles, the average volume-weighted diameter determined by TEM was $\sim 29$ Å with a full width at half maximum (FWHM) of $\sim 15$ Å. With reference to Figure 7.1, upon irradiation (at fluences of $6 \times 10^{13}$ and $1 \times 10^{14}$) the nanoparticle size distribution does not change appreciably. Further irradiation ($3 \times 10^{14}$) causes an apparent decrease in nanoparticle density as well as average size. After irradiation at $1 \times 10^{15}$, no nanoparticles are observable although the presence of Cu was confirmed by energy dispersive x-ray analysis. We infer that a fluence of $1 \times 10^{15}$ causes sufficient ion beam mixing to dissolve the
7.3. RESULTS AND DISCUSSION

Figure 7.1: TEM micrographs of Cu nanoparticle samples: (a) unirradiated, and after ion irradiation to a fluence of (b) $6 \times 10^{13}$, (c) $1 \times 10^{14}$, (d) $3 \times 10^{14}$, and (e) $1 \times 10^{15}$ /cm$^2$. Inset in (a) is a high-resolution image of an individual nanoparticle where the (111) lattice planes of fcc Cu are discernible.
nanoparticles in the matrix.

Figure 7.2(a) shows the measured SAXS profile (symbols) and corresponding fitted data (solid lines) for both unirradiated and irradiated nanoparticles. Minor changes in the SAXS profile are observed for irradiated nanoparticles up to a fluence of $3 \times 10^{14}$. For fluences $1 \times 10^{15}$ or greater the SAXS profile is similar to that of the as-implanted sample (not shown), consistent with the dissolution of the nanoparticles observed by TEM. Figure 7.2(b) shows the volume-weighted size distributions obtained by SAXS as a function of fluence. For the unirradiated sample, the distribution obtained from TEM is also included (columns)\(^1\). Table 7.2 summarizes the size distributions obtained from SAXS for irradiation fluences up to $3 \times 10^{14}$. A general increase in average volume-weighted diameter is observed with increasing irradiation fluence up to $2 \times 10^{14}$, indicating softening of the nanoparticle/matrix interface. At fluences where irradiation yields nanoparticle dissolution ($\geq 1 \times 10^{15}$) SAXS is featureless.

In summary, the nanoparticles were spherical (TEM) and of the fcc structure (electron diffraction) prior to ion irradiation. Following ion irradiation, the nanoparticles retained their spherical shape (TEM) while the average nanoparticle diameter increased (slightly SAXS) up to a fluence of $2 \times 10^{14}$. Residual crystallinity was not apparent (electron diffraction) after ion irradiation to a fluence of $1 \times 10^{14}$. Fluences greater than $3 \times 10^{14}$ yielded nanoparticle dissolution (TEM) into the matrix.

\(^1\)The slight discrepancy between the SAXS and TEM data is related to the inherent difficulty in resolving the smaller nanoparticle sizes in the microscope.
Figure 7.2: SAXS analysis and results: (a) SAXS profile and fitted data for the unirradiated nanoparticles and as a function of ion irradiation fluence (offset) and (b) the volume-weighted size distributions as a function of ion irradiation fluence (offset) including the size distribution determined by TEM for comparison (unirradiated sample only).
Table 7.2: SAXS results: volume-weighted average nanoparticle diameter as a function of ion irradiation fluence. The diameter errors were estimated by varying the width of the fitted $Q$ window by $\pm 5\%$.

<table>
<thead>
<tr>
<th>Fluence (cm$^{-2}$)</th>
<th>Nanoparticle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.5 ± .1</td>
</tr>
<tr>
<td>1x10$^{13}$</td>
<td>2.5 ± .1</td>
</tr>
<tr>
<td>3x10$^{13}$</td>
<td>2.5 ± .1</td>
</tr>
<tr>
<td>6x10$^{13}$</td>
<td>2.4 ± .1</td>
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<td>1x10$^{14}$</td>
<td>2.7 ± .1</td>
</tr>
<tr>
<td>2x10$^{14}$</td>
<td>2.8 ± .1</td>
</tr>
<tr>
<td>3x10$^{14}$</td>
<td>2.5 ± .1</td>
</tr>
</tbody>
</table>

7.3.2 LNT irradiation: atomic structure and intermixing

Figure 7.3(a) displays $k^3$-weighted EXAFS spectra for the as-implanted, unirradiated and bulk samples over the fitted $k$-range of 3.0 - 16.3 Å$^{-1}$. The much reduced amplitude for the as-implanted sample is consistent with the absence of nanoparticles. Upon annealing, the nanoparticle and bulk sample spectra are similar in shape though differ in magnitude due to the formation of Cu nanoparticles with fcc structure as discussed below. Figure 7.3(b) displays $k^3$-weighted EXAFS spectra for the nanoparticle samples as a function of ion irradiation fluence. Note the decrease in EXAFS amplitude with increasing fluence. For fluences of 1x10$^{15}$ and above, the spectra are comparable to that of the as-implanted sample consistent with dissolution of the nanoparticles.
Figure 7.3: $k^3$ - weighted EXAFS spectra for: (a) the unirradiated bulk standard, as-implanted Cu and unirradiated nanoparticle sample, and (b) the nanoparticle samples as a function of ion irradiation fluence.
Figures 7.4(a) and (b) show the FTs corresponding to spectra in Figures 7.3(a) and (b), respectively. As expected, the spectrum of the unirradiated nanoparticle sample is comparable, though of lesser magnitude, to that of the bulk fcc sample. The first three pronounced peaks correspond to the first three nearest neighbor shells surrounding a Cu atom (at \( r = \sim 2.5, 3.6 \) and 4.3 Å, respectively). The reduced amplitude is indicative of a reduced coordination number and/or increased Debye-Waller factor for the Cu nanoparticles. Both are a consequence of the increased surface-to-bulk ratio and the relaxation/reconstruction of the surface. Upon irradiation we observe a decrease in peak height and concurrent increase in FWHM of the first nearest neighbor, consistent with a further decrease in average coordination number and/or increase in Debye-Waller factor. This result represents a disordered phase, ion beam mixing and/or a decrease in nanoparticle size. We will argue below that a combination of these scenarios is present at a fluence of \( 1 \times 10^{14} \).

For an irradiation fluence of \( 1 \times 10^{14} \), the first nearest neighbor is still apparent, while the structure at higher \( r \) is much diminished. Eventually (at a fluence of \( \sim 1 \times 10^{16} \)) all nearest neighbors disappear and the spectrum is similar to that of the as-implanted sample. For irradiation fluences \( \geq 1 \times 10^{15} \), a peak between the Cu absorber and first nearest neighbor Cu scatterers appears at \( \sim 1.8 \) Å consistent with Cu-O bonding [125]. The dissolution of Cu in the matrix (TEM) yields an increase in Cu-O bonding at the expense of Cu-Cu bonding. The inset in Figure 7.4(b) shows the FTs of the unirradiated bulk standard compared to a selection of irradiated standards. Clearly, structural changes occurring in the bulk upon irradiation are negligible, consistent with the inability to amorphize a bulk elemental metal with ion irradiation [48].

The average coordination number, bond length, Debye-Waller factor, and the
Figure 7.4: Fourier-transformed EXAFS spectra for: (a) the unirradiated bulk standard, as-implanted Cu and unirradiated nanoparticle sample, and (b) the nanoparticle samples as a function of ion irradiation fluence (offset) with (inset) the bulk standard for selected ion irradiation fluences.
third cumulant for the first nearest neighbor are listed in Table 7.3 and presented in Figures 7.5(a) - (d). We note the significantly higher structural disorder (Debye-Waller factor) for the Cu nanoparticles prior to irradiation as compared to the bulk, indicating the influence of the surface atoms (approximately half the atoms are located at the surface). In general, bulk Cu is not affected by ion irradiation (up to a fluence equivalent to ~ 50 displacements per atom (dpa)) while the Cu nanoparticles exhibit a decrease in coordination number and concurrent increase in bond length, Debye-Waller factor and third cumulant. In particular, the bond length and Debye-Waller factor increase by ~ 0.5 and 24%, respectively, for an ion irradiation fluence of 1x10^{14} equivalent to ~ 0.16 dpa. Previously we reported similar results for ion irradiated Ge nanoparticles [52], which were rendered amorphous at ~ 0.01 dpa with an increase in the Debye-Waller factor by ~ 25 % (the bulk standard was rendered amorphous by irradiation equivalent to ~ 1 dpa). Furthermore, a positive third cumulant signifies a non-Gaussian bond length distribution skewed towards longer bond lengths again consistent with an amorphous phase [126] as previously reported for amorphous Fe [122]. The large decrease in coordination number can be attributed to several factors as discussed below.

Figure 7.6 shows dynamic ion irradiation simulations (TRIDYN [127]) for a 25 Å thick Cu film embedded at a depth of 0.6 μm within a SiO₂ matrix to estimate the degree of intermixing upon irradiation by 5.0 MeV ¹²⁰Sn ions. For visual simplicity the abscissa has its origin at the center of the Cu film. Fluences of 1x10^{14} - 1x10^{15} are shown and for the former only a slight decrease (~ 2%) in the Cu peak concentration is observed. While the FWHM does not increase appreciably, the interface is no longer a step-function consistent with intermixing and less-well-defined nanoparticle/matrix interfaces. On the other hand, at a
Figure 7.5: Ion irradiation fluence dependence of the four structural parameters of the first nearest neighbor shell of bulk and nanoparticle samples: (a) coordination number, (b) bond length, (c) Debye-Waller factor, and (d) third cumulant. The lines are included to guide the eye.
Table 7.3: Cu-Cu EXAFS results: Structural parameters of bulk Cu and Cu nanoparticle samples as a function of ion irradiation fluence extracted from first nearest Cu neighbor EXAFS analysis ($k^3$-weighted). The third cumulant was not measureable for the bulk standard. Legend: CN = coordination number, BL = bond length, DW = Debye-Waller factor, C3 = third cumulant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN (atoms)</th>
<th>BL (Å)</th>
<th>DW ($10^{-3}$ Å$^2$)</th>
<th>C3 ($10^{-5}$ Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirr. standard</td>
<td>12 (fixed)</td>
<td>2.539 ± 0.001</td>
<td>2.3 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>1x10$^{13}$</td>
<td>12.3 ± 0.7</td>
<td>2.540 ± 0.003</td>
<td>2.5 ± 0.5</td>
<td>-</td>
</tr>
<tr>
<td>3x10$^{13}$</td>
<td>12.0 ± 0.9</td>
<td>2.542 ± 0.002</td>
<td>2.5 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>6x10$^{13}$</td>
<td>12.4 ± 0.8</td>
<td>2.538 ± 0.003</td>
<td>2.5 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td>1x10$^{14}$</td>
<td>12.3 ± 0.6</td>
<td>2.541 ± 0.005</td>
<td>2.4 ± 0.6</td>
<td>-</td>
</tr>
<tr>
<td>2x10$^{14}$</td>
<td>11.9 ± 0.9</td>
<td>2.539 ± 0.003</td>
<td>2.4 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>3x10$^{14}$</td>
<td>12.2 ± 1.1</td>
<td>2.538 ± 0.006</td>
<td>2.3 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>Unirr. nanoparticles</td>
<td>10.1 ± 1.1</td>
<td>2.520 ± 0.006</td>
<td>4.9 ± 0.7</td>
<td>0.6 ± 8.0</td>
</tr>
<tr>
<td>1x10$^{13}$</td>
<td>8.5 ± 1.2</td>
<td>2.523 ± 0.008</td>
<td>4.9 ± 0.7</td>
<td>6.6 ± 9.9</td>
</tr>
<tr>
<td>3x10$^{13}$</td>
<td>6.5 ± 1.0</td>
<td>2.535 ± 0.009</td>
<td>4.6 ± 0.7</td>
<td>22.1 ± 10.8</td>
</tr>
<tr>
<td>6x10$^{13}$</td>
<td>6.0 ± 0.6</td>
<td>2.533 ± 0.006</td>
<td>5.4 ± 0.5</td>
<td>10.7 ± 7.9</td>
</tr>
<tr>
<td>1x10$^{14}$</td>
<td>5.4 ± 0.6</td>
<td>2.533 ± 0.006</td>
<td>6.0 ± 0.6</td>
<td>13.7 ± 8.9</td>
</tr>
<tr>
<td>2x10$^{14}$</td>
<td>3.5 ± 0.6</td>
<td>2.537 ± 0.014</td>
<td>5.7 ± 1.3</td>
<td>12.2 ± 18.8</td>
</tr>
<tr>
<td>3x10$^{14}$</td>
<td>3.1 ± 0.7</td>
<td>2.535 ± 0.014</td>
<td>5.2 ± 1.3</td>
<td>7.7 ± 18.2</td>
</tr>
</tbody>
</table>
7.3. RESULTS AND DISCUSSION

Figure 7.6: Dynamic TRIM (TRIDYN [64]) simulations of ion beam mixing in 25 Å Cu embedded in SiO$_2$ induced by 5.0 MeV Sn ion irradiation. Note that the abscissa has its origin at the center of the Cu film and that the irradiated spectra are shifted due to sputtering at the surface.

fluence of $1\times10^{15}$ we observe significant intermixing, for example the peak Cu concentration is reduced by $\sim 50\%$ and the FWHM is nearly doubled. An equally significant increase in both O and Si concentration is observed within the Cu film (not shown). This result is consistent with the ion-irradiation-induced dissolution of nanoparticles as presented above.

The presence of both Cu-Cu and Cu-O environments must be considered when interpreting the trends for the short-range atomic structure as determined by EXAFS. The ion-irradiation-induced production of Cu-O bonds will reduce the apparent average Cu-Cu coordination number of the Cu nanoparticles.$^2$

$^2$Note that Cu-O bonds will not affect the measured Cu-Cu bond length, Debye-Waller factor
unirradiated sample, we can apply the following approximation relating the average Cu-Cu coordination number \( CN_{ave} \) and diameter \( D \) for a spherical 12-fold coordinated nanoparticle [22]:

\[
CN_{ave} = 12 \left(1 - \frac{3}{2D} R_b\right)
\]

where \( R_b \) is the bulk bond length. Using the average diameter measured by SAXS and the bulk bond length measured by EXAFS, we calculate an average Cu-Cu coordination number of \( \sim 10.1 \) atoms in excellent agreement with the measured value. Correlating such results with XANES described below, we conclude that prior to irradiation all implanted Cu is incorporated in the nanoparticles (i.e. not dissolved in the matrix).

To determine the fraction of Cu atoms in oxide (Cu-O bonds) and metal (Cu-Cu bonds) environments after irradiation, analysis of the x-ray absorption near-edge structure (XANES) was undertaken. Figure 7.7 shows XANES spectra for the irradiated nanoparticles compared to that of the unirradiated nanoparticles and bulk crystalline samples. The difference in the latter two is attributed to finite-size effects. After irradiation with a fluence of \( 1 \times 10^{16} \) the XANES is consistent with Cu dispersed in SiO\(_2\) [92], exhibiting a characteristic pre-edge feature typical of Cu\(_2\)O [125]. We estimated the fraction of dispersed Cu by fitting the spectrum of each irradiated nanoparticle sample in the energy range 8.95 - 9.10 keV to a linear combination of the unirradiated and \( 1 \times 10^{16} \) spectrum. Examples of these fits are shown in Figure 7.8(a). Table 7.4 lists the results, which are also presented graphically in Figure 7.8(b). Clearly, the irradiated samples contain Cu atoms in two distinct phases, i.e. Cu oxides and/or nanoparticles. Shown is the fraction of Cu bound to Cu in the form of nanoparticles as a function of ion irradiation fluence. As expected, we observe a decrease in Cu-Cu fraction or third cumulant as presented in Figures 7.5(b) through (d).
or, equivalently, an increase in the Cu-O fraction, with increasing fluence. At $1 \times 10^{14}$ the fraction of dispersed Cu is $\sim 40\%$. Also displayed in Figure 7.8(b) is the evolution of the coordination number, as a function of irradiation fluence, after the Cu-O fraction has been taken into account. We observe that the latter saturates at $\sim 9$ atoms at $1 \times 10^{14}$. At $3 \times 10^{14}$ the influence of Cu-O EXAFS signal causes the measurement errors to increase significantly.

TRIM simulations show that the recoil energies of matrix and Cu atoms are sufficient to displace any of the constituent atoms by $\sim 3$ Å (approximately 1-2 bond lengths) [16], consistent with TRIDYN results and the less-well-defined nanoparticle/matrix interfaces. Additionally, the highly non-equilibrium nature of ion irradiation causes strong Si-O bonds to break. Cu atoms recoiled into the
Figure 7.8: (a) Irradiated Cu nanoparticle XANES spectra fitted with a linear combination of the unirradiated and $1 \times 10^{16}$ spectrum. (b) Cu-Cu fraction and coordination number (adjusting for the former) in the nanoparticles as a function of ion irradiation fluence.
Table 7.4: Cu-Cu bonding fraction as determined by XANES analysis. Note that an error of 5% was taken as a reasonable estimate [92]. The last column is the Cu-Cu coordination number within the remainder of the nanoparticle material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Cu-Cu CN (atoms)</th>
<th>Cu-Cu fraction (%)</th>
<th>Real Cu-Cu CN (atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirr. nanoparticles</td>
<td>10.1 ± 1.1</td>
<td>100 ± 5</td>
<td>10.1 ± 1.2</td>
</tr>
<tr>
<td>1x10^13</td>
<td>8.5 ± 1.2</td>
<td>100 ± 5</td>
<td>8.5 ± 1.3</td>
</tr>
<tr>
<td>3x10^13</td>
<td>6.5 ± 1.0</td>
<td>90 ± 5</td>
<td>7.2 ± 1.2</td>
</tr>
<tr>
<td>6x10^13</td>
<td>6.0 ± .6</td>
<td>70 ± 5</td>
<td>8.6 ± 1.1</td>
</tr>
<tr>
<td>1x10^14</td>
<td>5.4 ± .6</td>
<td>60 ± 5</td>
<td>9.0 ± 1.2</td>
</tr>
<tr>
<td>2x10^14</td>
<td>3.5 ± .6</td>
<td>40 ± 5</td>
<td>8.8 ± 2.3</td>
</tr>
<tr>
<td>3x10^14</td>
<td>3.1 ± .7</td>
<td>25 ± 5</td>
<td>12.4 ± 3.7</td>
</tr>
<tr>
<td>1x10^15</td>
<td>–</td>
<td>0 ± 5</td>
<td>–</td>
</tr>
<tr>
<td>3x10^15</td>
<td>–</td>
<td>0 ± 5</td>
<td>–</td>
</tr>
<tr>
<td>1x10^16</td>
<td>–</td>
<td>≡ 0</td>
<td>–</td>
</tr>
</tbody>
</table>
matrix will, under the minimum diffusion conditions present (LNT), preferentially bond with O rather than Cu (c.f. bond enthalpies for Cu-O and Cu-Cu [19]). The net effect of ion irradiation, viewed simplistically, but in agreement with XANES results presented above, is a reduction in diameter of the elemental Cu nanoparticles (cores) surrounded by an environment rich in Cu-O bonds. For the latter, the Cu oxidation state and local coordination is similar to that in Cu$_2$O, albeit not in a crystalline form, as determined by XANES analysis above [125]. At a fluence of 1x10$^{14}$, the metallic core has an average coordination number of 9.0 ± 1.2 atoms. We stress that the presence of Cu-O bonds do not contribute to the (average) Cu-Cu bond length, Debye-Waller factor, or third cumulant.

A crystalline Cu$_2$O standard (diluted powder) was also measured in EXAFS fluorescence mode. The first nearest neighbor consisting of two O atoms was analyzed and compared to that for the as-implanted and 1x10$^{16}$ sample. A $k^3$-weighting was applied and the first O coordination shell was then isolated by inverse transforming over a non-phase-corrected $r$ range of 0.6 - 2.0 Å. The results are summarized in Table 7.5 ($S_0^2$ and $E_0$ values were determined from the standard and kept constant thereafter). From TEM and XANES presented above, we know that a fluence of 1x10$^{16}$ leads to complete dissolution of the nanoparticles. From the EXAFS results presented in Table 7.5 we note that, as expected, both prior to the formation of nanoparticles and after dissolution of the nanoparticles there is predominantly Cu-O bonding. The local coordination and oxidation state is comparable to that of the Cu$_2$O standard.

The influence of ion irradiation on the short-range atomic structure is best illustrated by the radial distribution function (RDF). The RDFs were reconstructed from the first three cumulants of the Cu-Cu inter-atomic distance distribution following the method of Dalba and Fornasini [91] and using a photoelectron mean
7.3. RESULTS AND DISCUSSION

Table 7.5: Cu-O EXAFS results: Structural parameters for the first nearest O neighbor in a Cu$_2$O standard, the as-implanted sample and the 1x10$^{16}$ sample. Since O is a low-Z scatterer, $k^3$-weighting was applied to emphasize the Cu-O bonds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>BL</th>
<th>DW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O standard</td>
<td>2 (fixed)</td>
<td>1.82 ± .02</td>
<td>4.3 ± 2.6</td>
</tr>
<tr>
<td>As-implanted</td>
<td>1.9 ± .2</td>
<td>1.84 ± .01</td>
<td>6.3 ± 2.3</td>
</tr>
<tr>
<td>1x10$^{16}$</td>
<td>2.0 ± .3</td>
<td>1.84 ± .01</td>
<td>7.2 ± 2.8</td>
</tr>
</tbody>
</table>

free path of 8 Å. Figure 7.9 shows the reconstructed RDFs for the nanoparticles prior to and after ion irradiation (1x10$^{14}$) using the corrected Cu-Cu coordination number of 9.0 atoms for the latter, while the bond length, Debye-Waller factor and third cumulant are those listed in Table 7.3. The RDF of the unirradiated bulk is included as a reference and all RDFs are normalized to the number of nearest neighbors. Upon irradiation of the nanoparticles we observe the following, (1) a decreased Cu-Cu coordination number and increased Debye-Waller factor consistent with an amorphous phase and/or reduced size and (2) an increased bond length and positive third cumulant consistent with an amorphous phase but not with a reduced size [125]. We thus suggest the spectrum of the irradiated Cu nanoparticles represents the amorphous phase structure. For comparison, a theoretical prediction from a dense random packing model for an elemental amorphous bulk metal is included (relaxed Bernal structure [126]). The experimental and theoretical RDFs for the amorphous phase are consistent and the marked...
asymmetry in both spectra is readily apparent.

Even in the absence of ion irradiation, the minimum-energy crystallographic phase of Cu nanoparticles need not be fcc. Indeed, Reinhard et. al. reported that non-embedded Cu nanoparticles (2.0 - 2.5 nm diameter) prefer an icosahedral structure consistent with theoretical predictions [128]. The first nearest neighbor shell of the icosahedral structure is split into two shells at $r_1$ and $r_2$ where $r_2$ is $\sim$ 5% greater than $r_1$ [129]. The EXAFS measurements, as presented above, are not consistent with such a structure. The surrounding matrix may inhibit formation...
of the icosahedral structure.

In summary, though the unirradiated Cu nanoparticles and bulk standard have a common fcc structure, the former exhibits significantly higher static disorder relative to the latter. While ion irradiation induces negligible changes in the bulk standard, the structural parameters of the nanoparticles are perturbed significantly. The decrease in Cu-Cu coordination number and increase in bond length, Debye-Waller factor and third cumulant are all consistent with an amorphous phase. The corresponding RDF is markedly asymmetric and skewed towards longer bond lengths, consistent with a dense random packing model [126]. Under the appropriate conditions, ion irradiation thus yields disordering, then amorphization and dissolution of Cu nanoparticles.

7.3.3 LNT irradiation: recrystallization

The sample irradiated to a fluence of $1 \times 10^{14}$ was annealed at 350°C for 1 h in forming gas. Figure 7.10 shows the Fourier-transformed EXAFS spectra for the sample prior to irradiation, after irradiation and after annealing. XANES measurements for the same sample series are shown in the inset. Analysis of the latter showed a virtually unchanged Cu-Cu fraction of $\sim 60\%$ upon annealing ($58 \pm 5\%$). The amplitude of the annealed sample signal increases relative to the irradiated sample due to an increase in Cu-Cu coordination number and decrease in Debye-Waller factor. The amplitude of the annealed sample signal remains less than the unirradiated sample signal due to the continued presence of the Cu-O fraction. Table 7.6 lists the structural parameters for these samples. In summary, we observe that the structural parameters of the recrystallized and unirradiated samples are nearly identical, which demonstrates that (1) the amorphous phase has been recrystallized and (2) the parameters listed for the amorphous phase
Figure 7.10: Fourier-transformed EXAFS spectra for the nanoparticle sample prior to irradiation, after irradiation at a fluence of $1 \times 10^{14}$ /cm$^2$ and after subsequent reannealing at 350 °C. The inset shows XANES spectra for the same sample series.

did not result from the presence of recoiled lattice atoms.

The Cu nanoparticles investigated here were clearly perturbed, relative to the bulk standard, prior to irradiation. Though the fcc structure was retained, the inherent structural disorder (Debye-Waller factor) of the Cu nanoparticles was twice that of the bulk phase. The latter is the result of bonding distortions at the nanoparticle/matrix interface [130] and the concomitant increase in the nanoparticle structural energy. Given that approximately half the atoms reside at the interface, the influence of these bonding distortions is necessarily great, in
Table 7.6: Structural parameters of Cu nanoparticles prior to irradiation, after irradiation at a fluence of $1 \times 10^{14}$ cm$^{-2}$ and after subsequent reannealing at $350 \degree C$ extracted from first nearest neighbor EXAFS analysis ($k^2$-weighted).

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN (atoms)</th>
<th>BL (Å)</th>
<th>DW ($10^{-3}$ Å$^2$)</th>
<th>C3 ($10^{-5}$ Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirr. nanoparticles</td>
<td>10.1 ± 1.1</td>
<td>2.520 ± .006</td>
<td>4.9 ± .7</td>
<td>0.6 ± 8.0</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>9.0 ± 1.2</td>
<td>2.533 ± .006</td>
<td>6.0 ± .6</td>
<td>13.7 ± 8.9</td>
</tr>
<tr>
<td>Reannealed</td>
<td>10.3 ± 1.2</td>
<td>2.522 ± .005</td>
<td>4.9 ± 0.6</td>
<td>1.9 ± 8.5</td>
</tr>
</tbody>
</table>

marked contrast to the bulk standard. (This is also in contrast to the irradiation of $\sim 8$ nm diameter Cu nanoparticles where < 15% of the atoms reside at the surface for which an amorphous component was not observed [131]). The high surface-to-bulk ratio of the nanoparticles can account not only for the initially large Debye-Waller factor, but may also serve as a preferential site for the nucleation of the amorphous phase upon ion irradiation and/or stabilize such a phase subsequent to formation.

### 7.3.4 RT irradiation

Figures 7.11(a) through (c) show TEM images of the unirradiated, 6.0 MeV $^{120}$Sn and 6.0 MeV $^{74}$Ge irradiated samples, respectively. The spherical shape of the nanoparticles as well as the size distribution appears to be largely unaffected by the ion irradiations. SAXS measurements were performed to determine the distribution of sizes and volume-weighted average diameters. Figure 7.12(a) and (b) show SAXS intensity profiles and the extracted size distributions, respectively.
As qualitatively observed from TEM, the distribution is largely independent of the irradiation conditions. Table 7.7 summarizes the average volume-weighted nanoparticle diameters as extracted from SAXS. The average diameter was 2.5 nm prior to irradiation and is, in general, decreasing with increasing dpa values.

Figure 7.13 shows the Fourier transformed phase-corrected $k^3$ - weighted EX-AFS spectra for the nanoparticle samples. Inset is the bulk Cu film (prior to and after ion irradiation with 6.0 MeV $^{74}$Ge) as compared to the nanoparticle sample prior to irradiation. The three nearest neighbor atomic coordination shells are apparent at radial distances $r = \sim 2.2$, 3.4 and 4.2 Å, respectively, from the central Cu absorber. Again, the bulk spectrum after irradiation (for example 6.0 MeV $^{74}$Ge) was nearly identical to that for the unirradiated bulk, consistent with the high regeneration rate of the bulk elemental metallic structure [48]. Upon ion irradiation of the nanoparticle samples the short-range atomic structure is
Figure 7.12: (a) SAXS profiles for the nanoparticle samples before and after ion irradiation and (b) the corresponding nanoparticle size distributions. Graphs in both panels have been offset for clarity.
Table 7.7: SAXS results: volume-weighted average nanoparticle diameter for each ion irradiation condition. The diameter errors were estimated by varying the width of the fitted $Q$ window by $\sim \pm 5\%$.

<table>
<thead>
<tr>
<th>Ion irradiation</th>
<th>Cu dpa</th>
<th>Nanoparticle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>0</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>5.0 MeV $^{120}$Sn</td>
<td>0.16</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>6.0 MeV $^{120}$Sn</td>
<td>0.18</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>3.5 MeV $^{74}$Ge</td>
<td>0.20</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>6.0 MeV $^{74}$Ge</td>
<td>0.24</td>
<td>2.2 ± 0.1</td>
</tr>
</tbody>
</table>

altered. XANES revealed a pre-edge feature characteristic of Cu$^+$ dissolved in SiO$_2$ [92] for the irradiated nanoparticle samples, consistent with the presence of Cu-O bonds (not shown). Linear combination fits of oxidized and metallic phases, presented in Table 7.8, demonstrate a decreasing fraction of Cu-Cu bonding with increasing dpa values, consistent with dissolution of nanoparticles and the results presented in the previous section. Figure 7.14 plots the Cu-Cu fraction as a function of Cu dpa for both the LNT and RT irradiations. The results for the two studies are comparable, indicating that the irradiation temperature does not influence the dissolution of nanoparticles. In order to elucidate the relative influence of the nuclear and electronic stopping components consider for example the 6.0 MeV $^{74}$Ge irradiation at RT (indicated by an arrow in Figure 7.14). For this irradiation the electronic stopping component was nearly four times the nuclear (Table 7.1), while for the LNT irradiations the nuclear and electronic stopping components were near equal. This indicates that the nuclear stopping (expressed
in terms of the dpa) is the cause for the nanoparticle dissolution, consistent with bulk Cu (unlike some other bulk elemental metals) being insensitive to electronic stopping [132].

Structural parameters were extracted by EXAFS analysis of the first nearest neighbor coordination shell for both bulk and nanoparticle samples before and after ion irradiation. Table 7.9 summarizes the structural parameters and confirms quantitatively that the bulk film is unaffected by the irradiation. For the
Table 7.8: XANES results: fraction of Cu-Cu bonds for each ion irradiation condition. Note that an error of 5% was taken as a reasonable estimate [92].

<table>
<thead>
<tr>
<th>Ion irradiation</th>
<th>Cu dpa</th>
<th>Cu-Cu fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>-</td>
<td>0 ± 5</td>
</tr>
<tr>
<td>5.0 MeV $^{120}$Sn</td>
<td>0.16</td>
<td>70 ± 5</td>
</tr>
<tr>
<td>6.0 MeV $^{120}$Sn</td>
<td>0.18</td>
<td>63 ± 5</td>
</tr>
<tr>
<td>3.5 MeV $^{74}$Ge</td>
<td>0.20</td>
<td>68 ± 5</td>
</tr>
<tr>
<td>6.0 MeV $^{74}$Ge</td>
<td>0.24</td>
<td>47 ± 5</td>
</tr>
</tbody>
</table>

Figure 7.14: Cu-Cu fraction as a function of Cu dpa for both the liquid N$_2$ temperature (LNT) and room temperature (RT) ion irradiations.
nanoparticle samples the amount of Cu-O is taken into account for the tabulated coordination number. Upon ion irradiation with 5.0 MeV $^{120}$Sn (0.16 dpa) an increase in the Debye-Waller factor is observed. However, no bond length expansion or large positive third cumulant was found as previously seen for ion irradiation at LNT\(^3\). Although, in the present study, the Debye-Waller factor does not increase further for the higher dpa values, we observe that for 0.20 dpa (3.5 MeV $^{74}$Ge) and, in particular, 0.24 dpa (6.0 MeV $^{74}$Ge), there is a concomitant significant increase in both the bond length and third cumulant. These observations are comparable to those reported above for 5.0 MeV $^{120}$Sn ($1 \times 10^{14}$) at LNT and suggests the possible existence of an amorphous structure upon RT irradiations.

### 7.3.5 Thermal characteristics

The unirradiated nanoparticles and those irradiated with $1 \times 10^{14}$ 5.0 MeV $^{120}$Sn (0.16 dpa) at LNT were measured in EXAFS fluorescence mode as a function of measurement temperature (up to RT) and compared to the bulk Cu standard. $k^2$-weighted data was analyzed using the multiple fit approach outlined in Chapter 5 and using $k$ and $r$ ranges of 3.5 - 11 Å\(^{-1}\) and 1.64 - 2.84 Å, respectively. Figure 7.15(a) shows the temperature dependence of the Debye-Waller factor for all samples. The extracted values for $\Theta_E$ are given in the plot.

The unirradiated sample (2.5 nm nanoparticles) exhibits a smaller $\Theta_E$ compared to the bulk value. This finding is consistent with the previous result for the 3.3 nm nanoparticle sample, which also exhibited a smaller $\Theta_E$ (Chapter 5).

\(^3\)We note that at RT (as compared to LNT) the ion-irradiation-induced crystalline-to-amorphous phase transformation in semiconductors, for example bulk Si [133], requires about four times the dpa.
Table 7.9: Cu-Cu EXAFS results: Structural parameters of bulk Cu and Cu nanoparticle samples for each ion irradiation condition (Cu dpa) extracted from first nearest Cu neighbor EXAFS analysis ($k^2$-weighted). The third cumulant was not measurable for the bulk standard. Note that for the Cu nanoparticles the coordination numbers have been adjusted to account for the amount of Cu-O in the matrix as determined by XANES analysis. Legend: CN = coordination number, BL = bond length, DW = Debye-Waller factor, C3 = third cumulant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>BL</th>
<th>DW</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cu dpa) (atoms) (Å) (10⁻³ Å²) (10⁻⁵ Å³)</td>
<td></td>
<td></td>
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<tr>
<td>Unirr. standard</td>
<td>12 (fixed)</td>
<td>2.542 ± .001</td>
<td>2.7 ± .1</td>
<td>-</td>
</tr>
<tr>
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<td></td>
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<td></td>
</tr>
<tr>
<td>0.16</td>
<td>12.2 ± .4</td>
<td>2.540 ± .001</td>
<td>2.8 ± .2</td>
<td>-</td>
</tr>
<tr>
<td>0.18</td>
<td>12.2 ± .5</td>
<td>2.541 ± .001</td>
<td>2.9 ± .2</td>
<td>-</td>
</tr>
<tr>
<td>0.20</td>
<td>12.3 ± .5</td>
<td>2.538 ± .002</td>
<td>2.8 ± .2</td>
<td>-</td>
</tr>
<tr>
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<td>11.9 ± .3</td>
<td>2.541 ± .001</td>
<td>2.7 ± .1</td>
<td>-</td>
</tr>
<tr>
<td>Unirr. nanoparticles</td>
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<td>2.525 ± .004</td>
<td>5.6 ± .4</td>
<td>2.7 ± 5.7</td>
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<tr>
<td>Irradiated:</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.16</td>
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<td>2.528 ± .008</td>
<td>6.4 ± .8</td>
<td>1.7 ± 11.1</td>
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<tr>
<td>0.18</td>
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<tr>
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<td>6.4 ± .8</td>
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</tr>
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<td>0.24</td>
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<td>2.552 ± .007</td>
<td>6.5 ± .8</td>
<td>28.0 ± 10.1</td>
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Figure 7.15: (a) Temperature dependence of the Debye-Waller factor for the bulk standard as well as for the unirradiated and irradiated nanoparticle samples. (b) Relative variation of the Einstein temperature of the nanoparticle samples (combined results from Chapter 5) from that of the bulk standard. The solid line is included to guide the eye. The dotted line shows the relative Einstein temperature for the irradiated nanoparticle sample.
With decreasing nanoparticle size two opposing effects influence the $\Theta_E$ value. These effects are:

1. the SBR, which increases and shifts the $\Theta_E$ to a smaller value.

2. the capillary pressure, which increases and shifts the $\Theta_E$ to a greater value.

From our results, the unirradiated nanoparticles of 2.5 and 3.3 nm diameter both exhibit a reduced $\Theta_E$ indicating that the SBR effect dominates over the pressure effect for nanoparticles prior to irradiation. Meanwhile, the irradiated sample exhibits an intermediate $\Theta_E$, which is greater than that for the unirradiated sample, but smaller than for the bulk standard. Previously, we argued that upon irradiation Cu monomers are produced in the matrix in the vicinity of a Cu core. Thus, simply from a reduction in Cu nanoparticle (core) size, the value for $\Theta_E$ would be expected to decrease further upon irradiation (when the SBR effect dominates). This point of view is represented graphically in Figure 7.15(b). It shows the decrease in $\Theta_E$ for the unirradiated nanoparticle samples (2.5 nm presented in this chapter and 3.3 and 14.0 nm presented in Chapter 5) relative to the bulk standard. The latter is included in the plot with a relative decrease of 0%. The dotted line shows the relative decrease in $\Theta_E$ for the irradiated nanoparticles. Clearly, this value is not consistent with a trend purely governed by the SBR as argued above.

Indeed, the thermal response of the irradiated sample is markedly different from that expected of small Cu nanoparticles (exhibiting the fcc atomic structure). This finding is consistent with the Cu atomic structure, after ion irradiation, being markedly different from that prior to irradiation. As argued earlier, this structure is comparable to an amorphous metallic phase. In fact, molecular dynamics simulations indicate that while $\Theta_E$ of polycrystalline (8.2 Å) Cu
is $\sim 11\%$ less than that of the bulk fcc structure, amorphous Cu exhibits a $\Theta_E$ depression of only $\sim 7\%$ \cite{33}.

Figure 7.16 shows the bond length, bond length variation and third cumulant as a function of measurement temperature for the nanoparticle and bulk samples. The bond length variation is defined as the change in bond length for each sample compared with the lowest temperature measurement. Similarly to our results presented above, the temperature dependent bond length and third cumulant for the amorphous phase are different from that of the unirradiated nanoparticles. Specifically, the temperature dependent increase is more rapid for the amorphous sample. Figure 7.16(b) indicates a greater thermal expansion coefficient present for the irradiated nanoparticles consistent with the greater asymmetry shown in Figure 7.16(c) \cite{29, 30}.

7.4 Summary

In conclusion, we have investigated the atomic structure of ion irradiated Cu nanoparticles synthesized in SiO$_2$ by ion implantation and thermal annealing. Prior to irradiation, all Cu was in the form of nanoparticles exhibiting the fcc structure though the inherent structural disorder was twice that of the bulk. Upon irradiation at liquid N$_2$ temperature the fcc order vanished while the fraction of dissolved Cu atoms increased due to collisional mixing. The amount of oxide increased until the nanoparticles were completely dispersed in the matrix at fluences $\geq 1\times 10^{15}$ cm$^{-2}$ ($\geq 1.6$ dpa). At an intermediate fluence of $1\times 10^{14}$ cm$^{-2}$ (0.16 dpa), the Debye-Waller factor of the first nearest neighbor shell increased by $\sim 25\%$. Simultaneously, the bond length and third cumulant increased while

\footnote{Averaged values for $\Theta_E$ were based on Figure 18 of Wang et al \cite{33} or equivalently Figure 1.11 in Chapter 1.}
Figure 7.16: Temperature dependence of the bond length and third cumulant for the bulk standard and unirradiated and irradiated nanoparticle. In (b) the bond length variation, as compared to the lowest temperature bond length for each sample, is shown.
the Cu-Cu coordination number decreased. Such observations are consistent with a dense random packing model for amorphous elemental metals. Moreover, after the amorphized sample was annealed at 350 °C for 1 h (insufficient for nanoparticle growth), the initial pre-irradiation structure was recovered.

Ion irradiations performed at RT showed that the temperature did not appreciably influence either the dissolution of nanoparticles or their resulting short-range atomic structure. The RT results also indicated that nuclear stopping, as opposed to electronic, causes the extreme sensitivity to ion irradiation observed for the nanoparticles.

Temperature dependent EXAFS measurements of the unirradiated and irradiated (1x10^{14} cm^{-2} at liquid N_{2}) nanoparticle samples were compared to the bulk standard. It was found that prior to irradiating the nanoparticles, the thermal component of the disorder increased faster than for the bulk, consistent with the finite size of the former. Meanwhile, the trend for the irradiated sample was not consistent with the nanoparticle size indicating that the structure of these nanoparticles deviate from the fcc structure.

The following chapter contains the conclusions and suggestions for further research.
Chapter 8

Conclusions

This chapter contains conclusions of the research presented in this thesis and some directions for future work.
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CHAPTER 8. CONCLUSIONS

8.1 This work

Metallic nanoparticles (Cu and Zn) were formed in amorphous SiO₂ by ion implantation and thermal annealing. The formation of nanoparticles and the nanoparticle short-range atomic structure was studied as a function of synthesis parameters and nanoparticle size for both species. Cu nanoparticles were then irradiated with ions sufficiently energetic to have a projected range beyond the nanoparticle layer. For this study the short-range atomic structure was measured as a function of ion irradiation fluence. The key findings of the studies are summarized below.

Formation of Cu nanoparticles

Cu ions were implanted into 5 μm SiO₂ to maximum concentrations of 0.3, 1.0, 3.2 and 8.6 at.%. The samples were then annealed at 500, 800 and 1100 °C for one hour in a non-oxidizing atmosphere.

It was found that the combination of low Cu concentration and high annealing temperature caused loss of Cu (evaporation through the surface). Meanwhile, for the highest concentrations, nanoparticles were formed already prior to annealing. Evidently, the formation of nanoparticles was correlated with the temperature-dependent solubility of Cu in the SiO₂.

For those samples were a fraction of Cu atoms were still dissolved in the matrix (notably the low concentration and low annealing temperature samples) the Cu preferred a local coordination and oxidation state similar to that in Cu₂O, albeit not in crystalline form.

The formed nanoparticles were found to be spherical (up to ~30 nm in diameter depending on synthesis conditions) and single crystalline, exhibiting the fcc structure. However, EXAFS measurements revealed that the short-range atomic
structure deviated from that of the bulk reference. Four structural parameters of
the first nearest neighbor were measured, specifically the coordination number,
bond length, Debye-Waller factor and the third cumulant of the radial distri-
bution function. Generally, all four parameters were both concentration- and
annealing temperature dependent. The largest deviations, as compared with the
bulk, were found for low concentrations and low annealing temperatures. For
high concentrations and high annealing temperatures, the four parameters were
comparable to those of the bulk reference. Specifically, for the nanoparticle sam-
pies as compared with the bulk, both the coordination number and bond length
were suppressed. Meanwhile, the Debye-Waller factor was greater than for the
bulk and the radial distribution function was non-Gaussian (that is a non-zero
third cumulant). All these findings symbolize the influence that the reconstructed
surface with under-coordinated atoms has on the short-range atomic structure of
the nanoparticle as a whole.

Equivalently, the four structural parameters were nanoparticle-size dependent.
A linear dependence between the increased Debye-Waller factor (as compared
with the bulk) and the inverse nanoparticle diameter showed that not only does
the disorder increase with decreasing nanoparticle size, but this disorder is pre-
dominantly located at the surface. For example, for a nanoparticle 3 nm in
diameter the Debye-Waller factor was 70% greater than that of the bulk. Mean-
while, the bond length was suppressed as compared with the bulk. For example,
for a 3 nm nanoparticle, the bond length contraction was 0.7%. The bond length
contraction increased with decreasing nanoparticle size. From these results, the
nanoparticle surface tension was measured to be $2.5 \pm 0.4 \text{ J/m}^2$. This surface
tension, corresponding to several GPa pressure on the core of the nanoparticle,
is caused by the surface curvature, but is greater than that measured for free-
Temperature dependent EXAFS measurements (from 15K to room temperature) revealed that the Einstein temperature decreased with decreasing nanoparticle size. The Einstein temperature is a measure of lattice stiffness and a decrease in the Einstein temperature implies a weaker Cu-Cu bond environment. For example, the Einstein temperature of 3.3 nm nanoparticles was 8% smaller than that of the bulk, while large nanoparticles of 14.0 nm were unaffected. The decreased Einstein temperature found for the smaller nanoparticles is consistent with the increased fraction of under-coordinated surface atoms.

### Formation of Zn nanoparticles

Zn ions were implanted into 0.6 μm SiO₂ to maximum concentrations of 3.2 and 6.4 at.%. The samples were then annealed at 400, 600 and 800 °C for one hour in a non-oxidizing atmosphere.

It was found that an annealing temperature of 600 °C was required to form nanoparticles. These nanoparticles were spherical, ~ 3 nm in diameter and single crystalline exhibiting the hcp structure. However, at 600 °C there was still a significant fraction of Zn dissolved in the matrix. The formation of nanoparticles was found to be independent of the implanted Zn concentration.

Upon annealing at 800 °C the average nanoparticle diameter grew to 4 - 5 nm due to the formation of a small number of large nanoparticles (up to 25 nm). These large nanoparticles also exhibited the hcp structure. Again, the formation of these nanoparticles was found to be independent of the implanted Zn concentration.

For the bulk hcp structure the two first nearest neighboring coordination shells are separated by ~ 0.3 Å and contain 6 atoms each. For the implanted samples
annealed at 800°C the nanoparticles were determined to have a fully occupied first nearest neighbor coordination shell, while the second nearest neighbor was suppressed compared with the bulk. This finding could not be explained. Concurrently, the Debye-Waller factor was greater in the second shell as compared with the first, both for the bulk standard and nanoparticle samples. This observation, correlated with that for the coordination numbers, indicated parameter correlation and thus the EXAFS measurements were inconclusive. The parameter correlation potentially stems from the closeness of the two shells.

**Ion irradiation of Cu nanoparticles**

Cu ions were implanted into 2 μm SiO₂ to a maximum concentration of 3.6 at.% and annealed at 650°C for one hour in a non-oxidizing atmosphere. The samples were then either irradiated with 5.0 MeV Sn ions at liquid N₂ temperature or at a variety of ion/energy combinations at room temperature. A bulk standard was irradiated simultaneously.

Upon annealing the implanted sample, spherical nanoparticles of average diameter 2.5 nm exhibiting the fcc structure were formed. In terms of short-range atomic structure, the nanoparticles exhibited a suppressed coordination number, bond length contraction and an increased Debye-Waller factor consistent with the previous results. Upon irradiation with Sn ions at liquid N₂ temperature the nanoparticle size remained largely constant up to a fluence of 3x10^{14} cm⁻². At higher fluences the nanoparticles dissolved completely in the matrix, forming Cu-O bonds. In fact, the fraction of Cu-O bonds increased gradually from 0% prior to irradiation to 100% at the highest fluences (above 3x10^{14} cm⁻²). EXAFS spectroscopy showed that at an intermediate fluence of 1x10^{14} cm⁻² (corresponding to 0.16 displacements per atom - dpa), the short-range atomic structure of
the nanoparticle fraction was comparable to that expected for an amorphous metallic phase and *inconsistent* with finite-size effects alone as determined by the formation study above. Specifically, the atomic structure of the irradiated nanoparticles comprised a bond length expansion, a further increase in the Debye-Waller factor and a positive third cumulant. The bulk standard was unaffected by the irradiations.

For the room temperature irradiations it was found that, again, with increasing dpa values the nanoparticles were gradually dissolved into the matrix. The study also indicated that the nuclear stopping, as opposed to electronic, causes the extreme sensitivity to ion irradiation observed for the nanoparticles. An atomic structure comparable with that expected for an amorphous metallic phase, was observed upon irradiations corresponding to 0.20 dpa or above.

Temperature dependent EXAFS measurements (from 19K to room temperature) were performed on the nanoparticles before irradiation and after irradiating at liquid N\textsubscript{2} (0.16 dpa) and compared with the bulk standard. Similar to the results from the formation study, the Einstein temperature of the nanoparticles prior to irradiation was suppressed by 9%. Meanwhile, the Einstein temperature *increased* after irradiation, consistent with the post-irradiation atomic structure being markedly different from that prior to irradiation. This finding imply that while the structural disorder is greater in the amorphous state, the thermal disorder component increase with temperature is slower than that for the fcc nanoparticles.
8.2 Future directions

The findings presented in this thesis can form the basis for a number of projects, including:

- **Free-standing nanoparticles:** By analyzing the short-range atomic structure of free-standing nanoparticles the influence of the matrix can be quantified. These nanoparticles can be formed by for example evaporation techniques.

- **Melting of nanoparticles:** It would be interesting to study the melting point characteristics of embedded and free-standing nanoparticles. Though several studies have been undertaken to characterize for example melting point depression and melting point hysteresis of nanoparticles, there is still discussion as to what is the atomic structure of, for example, the supercooled or superheated phase of nanoparticles.

- **Optical properties:** As a continuation to the ion irradiation study it could prove interesting to measure the optical properties of metallic nanoparticles before and after ion irradiation.
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Clarifications:

**Solubility limit for Cu in SiO$_2$ (Chapter 5)**
The solubility limit for Cu in SiO$_2$ at room temperature, as stated on page 87, is $\sim 10^{12}$ atoms/cm$^3$ [Reference 97, Bibliography]. At elevated temperatures the solubility necessarily increases and at 1100°C (the highest annealing temperature) the solubility limit is $>10^{20}$ atoms/cm$^3$. The lowest concentration Cu implantation yielded $\sim 10^9$ atoms/cm$^3$ or well above the room temperature solubility limit. However, upon thermal annealing Cu gradually diffused out of the SiO$_2$ (either towards the Si/SiO$_2$ interface or the SiO$_2$ surface) as observed by RBS. These results were discussed in section 5.3.

**Figure 5.2 (Chapter 5)**
A color scheme has been implemented to distinguish the superimposed graphs:

![Graph](image)

**Figure 5.4(a) inset (Chapter 5)**
The inset has been changed to highlight an observed lattice spacing of (2.1±0.2) Å consistent with the nominal Cu(111) lattice spacing of 2.09 Å. Note that there are eight interplanar spacings between the solid black lines.
Cu bonding to the matrix constituents (Chapters 5, 7)
The candidate concluded that Cu-Si bonds are not present in the nanoparticle samples. The following supports this conclusion: Cu-Si bonds were not observed from analyzing the XANES or EXAFS data, while Cu-O bonds were. Given that the enthalpy of the Cu-O bond is greater than that of Cu-Si [webelements.com], Cu atoms dissolved in the matrix would prefer to bond to O.

Cu oxide standards for EXAFS (Chapter 5,7)
For the EXAFS measurements, oxide standards were diluted with boron nitride to yield a Cu concentration comparable to the nanoparticle samples. The appropriate amount of bulk Cu oxide was weighed and ground with a mortar and pestle together with boron nitride and then packed into an EXAFS sample cell.

Third cumulant of Cu nanoparticles (Chapters 5,7)
In the formation study the third cumulant of the nanoparticles is negative and of a greater absolute value for small nanoparticles as compared with large. In the irradiation study the nanoparticles prior to irradiation has a third cumulant near zero. While this could stem from an unexplored difference between the nanoparticles, it does not invalidate the fact that upon irradiation the third cumulant increases consistent with amorhization.

Formation parameter dependence for Zn nanoparticles (Chapter 6)
On page 128 the candidate states that “...neither the concentration or annealing temperature appreciably influence the average nanoparticle size. However...the annealing temperature does influence the nanoparticle size distribution”. This statement is not correct. In fact, the average nanoparticle diameter increases by ~ 50% upon annealing (from 600 to 800°C) while the implanted concentration, correctly, has little effect. (Never-the-less, one could argue that given the drastic change in nanoparticle size distribution upon annealing (at 800°C nanoparticles of up to 20 nm or larger are formed – these are ~ 500% larger than the average at 600°C) the change in average nanoparticle diameter is modest.)

Zn WAXS profiles (Chapter 6)
The widths of the diffraction peaks of the Zn nanoparticles are comparable to those of the corresponding film (Fig. 6.4) given that the probed nanoparticle ensembles are dominated by large diameters of up to ~ 20 nm (bulk-like nanoparticles).

Cu SAXS profiles (Chapter 7)
The candidate notes that in Fig. 7.2(a) the plots are for the raw SAXS profiles less the unimplanted SiO₂. Given that the 1×10¹⁵ ions/cm² profile was comparable to the unimplanted sample their difference was not included in Fig. 7.2(a).

Arguments for the formation of amorphous Cu nanoparticles (Chapter 7)
The results presented for the irradiation of Cu nanoparticles are consistent with the formation of an amorphous Cu phase. The candidate notes that upon irradiation (at 1×10¹⁴ ions/cm²) the decrease in coordination number and concomitant increase in Debye-Waller factor, bond length and third cumulant are all consistent with the formation
of an amorphous phase (Fig. 7.9 and discussion). Moreover, low temperature annealing (insufficient for nanoparticle growth) of the amorphous Cu returned the nanoparticles to the initial pre-irradiation structure.

Typing and minor corrections:

Page 4: Fig. 1.2 source is A.P. Alivisatos, J. Phys. Chem. 100 (1996) 13226.
Page 6: "...presence of Cu and Ag nanoparticles, respectively [6]."
Page 7: Fig. 1.4 source is Nanometals: formation and color, L.M. Liz-Marzán in Materials Today February 2004.
Page 30: "...electrons in the K, L, M, etc, shells of the absorbing atom."
Page 46: "...a surface barrier detector fixed at a scattering angle close to 180°."
Page 50: Fig. 3.4 source is Reference 30, Bibliography.
Page 60/62: "The monochromatic (x-ray) beam enters from the left...".
Page 61: in Section 3.6.3 note that Bragg’s Law (Equation 3.5) is just one aspect of the scattering of x-rays by matter and does not encompass inelastic effects, dynamic diffraction and x-ray reflectivity, for example.
Page 73: Note that splines, by construction, have continuous derivatives at the knots.
Page 79: "The window is overlayed the first theoretical FEFF path."
Page 81: $\chi(k)$ is given by $\sum_{\pi} \frac{(2ik)^\pi}{\pi!} C_n$ (Reference 61, Bibliography).
Page 89: Fig. 5.1 should refer to Table 5.1 for a list of the implantation energies.
Page 91: "...in samples with a low Cu concentration, there are less precipitation sites..."
Page 118: "For the 3.3 nm nanoparticles sample..."
Page 126: "...region where there are fewer structural defects in the matrix (that is beyond the implanted range)." Please compare this with Fig. 1.6.

Reference 16 (Bibliography): "The Stopping and Range of Ions in Solid."

Updated list of publications by the candidate:

Journal Publications

March 2008: Errata
Ion Beam Formation and Modification of Metallic Nanoparticles, Bernt Johannessen


March 2008: Errata

Ion Beam Formation and Modification of Metallic Nanoparticles, Bernt Johannessen


Refereed conference publications


Other publications
