PHASE STABILITY IN METALLIC MULTILAYERS

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* * * * *

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ABSTRACT

As the thin film materials used in electronic and optical applications continue to decrease in thickness to the nano-scales, marked changes in functional properties are expected to occur due to changes in crystal structure of these materials. Therefore, such multilayer systems have been of considerable interest due to the ability to control properties by engineering the structure of materials at these scales. The new characterization tools allow direct imaging and analysis of such materials in order to link the performance variations with the crystal structure variations.

Transmission Electron Microscopy (TEM) has been often the technique of choice in characterization of nanomaterials enabling not only imaging the structure of the material but also chemically probing of the composition changes at a high spatial resolution. The ultimate resolution achievable in the electron microscope is a product of both microscope and the specimen and the simultaneous effect of each defines the quality and quantity of the information transferred through the microscope. In this sense, the common ion-beam assisted TEM sample preparation techniques have been deeply recognized as being surface damaging at high ion milling energies (>5kV) thus limiting the information transfer in the microscope. For the first time, a low energy (<2kV) focused Ar ion beam milling system has been applied to remove the surface artifacts created by the high energy conventional broad Ar or focused Ga beam milling techniques. The overall quality of the samples drastically improved after the application
of the low energy milling practices and the outcome results directly enhanced the clarity of the information gathered at the atomic and nanoscale by the electron microscope.

Besides the specimen the resolution achievable in the electron microscope is strongly limited by the imperfections in the electron optics of the microscope column such as the spherical aberration of the electromagnetic lenses. Recently this problem has been solved by the correction of the spherical aberration of the microscope using a set of non-round lenses and consequently the information limit in an aberration corrected microscope (<0.1nm) has been pushed beyond an uncorrected microscope (~0.13nm). In 2007, such a corrector system in the probe-forming lens of a Scanning TEM microscope was successfully installed at The Ohio State University. The preliminary results from this microscope were presented in the content of this work where we have studied the microscope and performed first hand experiments.

Finally we have addressed the phase stability in Cu/Nb and Ti/Nb nanoscale metallic multilayers by extensive use of these advance characterization techniques and tools. At reduced layer thickness (<2nm) the change in fcc to bcc phase in Cu and hcp to bcc phase in Ti were experimentally confirmed using X-ray diffraction electron diffraction and electron imaging techniques along the plan-view and cross-section directions. These structural transformations were often referred to as being thermodynamic in nature and a classical thermodynamical model explains and predicts the formation of such pseudomorphic phases through the competition of volumetric and interfacial free energy variables. We have investigated both the structural and chemical changes in the Cu/Nb and Ti/Nb nanoscale metallic multilayers as a function of length scale in order to understand and predict the phase stability. The important constituents:
volumetric free energy and interfacial energy changes were experimentally derived considering the chemistry and structure of the multilayers and competition between these thermodynamic terms well explains the observed structural changes in nanoscale metallic multilayers.
Dedicated to my family
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CHAPTER 1

PHASE STABILITY IN
NANOSCALE METALLIC MULTILAYERS

1.1. Introduction

When thin films are deposited on suitable substrate surfaces, they can exhibit crystal structures that would be metastable for the same materials in their room temperature bulk form. In the literature, there have been many instances reporting such transformations in the case of either single film or multilayer stacks of two elements grown on single crystal substrates. For example *hexagonal closed pack (hcp)* to *body centered cubic (bcc)* transformation of Co grown on (110) GaAs is a good example for the case of a single layer deposited on a single crystal substrate [1]. Room temperature stable form of Co is *hcp* however when deposited as a thin layer (357Å thick) on a (110) GaAs substrate it adopts to metastable structure of *bcc* phase. In this case *bcc* Co exhibits interesting ferromagnetic properties very similar to that of α-Fe. Multilayers represent the stack of alternating single films grown on a single crystal substrate. In many occasions, multilayers show a unique orientation relationship either with the substrate that they are grown on or within each other regardless of the substrate. Consequently, results from many metal/metal systems have been reported in the literature, including Ti/Al, Nb/Zr, Nb/Ti and Co/Cr [2]. Experimental observations on multilayer systems have illustrated
cases where either one or multiple layers can exist with metastable structures, for example; \textit{fcc} Ti in Ti/Al multilayers, \textit{bcc} Zr and \textit{hcp} Nb in Nb/Zr multilayers and \textit{bcc} Co and \textit{hcp} Cr in Co/Cr multilayers [2,3].

In general, these metastable structures exist on the nanometer or sub-nanometer regime and the factors underlying these transitions are widely regarded as being thermodynamic in nature. Dregia et al have described a model based on classical thermodynamics that predicts the phase stability of metastable phases in thin films [4]. In this model, metastable phases are stabilized by the competition between the volumetric and interfacial energy components of the total free energy. Validity of this thermodynamic approach has been addressed in various metallic multilayer systems such as in Ti/Al, Ti/Nb and Zr/Nb multilayers where the formation of metastable phases was predicted and experimentally confirmed [2,3].

The key thermodynamic variables that aim to explain these transformations are often affected by the structural and composition of properties of these materials at the nanoscale (1nm = 10^{-9}m). For instance, compositional variations observed in the form of elemental intermixing or alloying alter the volumetric free energy change of the layers, whereas the interface atomic registry between the layers defines the interfacial free energy change. Hence the success in prediction and understanding of such materials phenomena can be strongly attributed to the capability of characterizing these properties at the nano-length scale. This eventually brings the need for using state-of-the art characterization tools that offer the highest spatial resolution for both imaging and chemical analysis of these fine structures.
For the first time, this dissertation will discuss the phase stability of \textit{bcc} Cu in the Cu/Nb multilayer and \textit{bcc} Ti in the Ti/Nb metallic multilayer systems, considering the variations not only in the crystal structure but also in the chemical composition of the layers. This thesis is organized as follows; Chapter 1 is the critical literature review of the thin film growth methods and describes the important aspects of the classical thermodynamical model in comparison with other proposed models. Chapter 2 briefly explains the basic fundamentals of high-resolution imaging (aberration-corrected imaging) and chemical analysis techniques that are employed in characterization of nanomaterials. This chapter also gives a detailed picture of a new low energy Ar ion beam TEM sample preparation technique. Chapter 3 provides the first results from a TEM sample preparation technique and also from an aberration-corrected STEM microscope. Chapter 4 addresses the phase stability in Cu/Nb and Ti/Nb multilayer systems. And finally Chapter 5 provides a summary of the experimental research results and suggests future directions.

\textbf{1.2. Thin Film Deposition Process}

Sputtering is one of the most widely used physical vapor deposition (PVD) techniques in producing thin films and it’s the main deposition process used in the thin film applications discussed in this work.

In a typical sputtering process, atoms are ejected from a negatively charged solid (cathode-target) by bombarding the surface with energetic ions, typically Ar$^+$. These emitted atoms traverse a reduced pressure atmosphere and deposit atomically on a
substrate (anode) to form the film [5]. The working gas, Ar, serves as the medium (plasma) in which an electrical discharge is initiated and sustained. The bombardment of the target occurs through the momentum transfer of the positive gas ions to target atoms [6]. As the sputtered atoms continue to condense and migrate on the substrate surface, different thin film growth modes occur. Depending on substrate free surface energy, $\gamma_s$, film free surface energy, $\gamma_f$, and substrate-film interface energy, $\gamma_i$, these thin film growth modes can be categorized as; island mode, layer mode and layer-island mode [7]. These modes are simply illustrated in Fig.1.1. In all these cases it is assumed that there is enough surface diffusion to minimize $\gamma$, and also nucleation is not limited by any chemical reactions or interdiffusion.

The criteria for the occurrence of the three modes can be described by the following inequalities:

- $\gamma_s < \gamma_i + \gamma_f$ Island Mode
- $\gamma_s \geq \gamma_i + \gamma_f$ Layer Mode (Small strain energy)
- $\gamma_s \geq \gamma_i + \gamma_f$ Layer-Island Mode (Large strain energy)

When there is not sufficient bonding between substrate and film to reduce $\gamma_i$, film does not wet the surface and smallest stable clusters nucleate and form three-dimensional islands. This growth mode is called the Volmer-Weber (V-W) or island mode [7]. Island growth is the common growth mode for metals deposited on oxide substrates. In layer growth mode (or Frank-Van der Merwe Mode), atoms in the film are more strongly bounded to the substrate than each other. The film forms a stable nucleus in two dimensions as planar sheets on the substrate and atomic layer-by-layer growth occurs [7]. The third growth mode, layer-island mode (or Stranski-Krastanov (S-K) mode), is a
Figure 1.1 Thin film growth modes [7].
combination of layer mode and island mode where growth starts with layer mode, and changes after a monolayer or two to island mode. This transition from two to three-dimensional growth is explained by the accumulation of large strain energy, which is introduced to the film layer due to the film-substrate mismatch [7].

Once initial nuclei have formed, coalescence occurs through the migration and rotation of the nuclei on the substrate [8]. During this process mobile atoms also migrate from smaller nuclei to larger ones and the nuclei become larger and fewer with time. This process is analogous to the Ostwald ripening process, which is widely referred in bulk metallurgy to explain grain growth by annealing [8].

After a continuous film has grown, cluster coalescence dominates the structure of the film and larger clusters, which may not necessarily be in contact with smaller clusters, grow at the expense of the smaller ones [9]. As the film develops, growth texture and preferred orientation occurs by the minimization of the surface free energy of the growing planes.

1.3. Epitaxy and Pseudomorphism

During the early stages of the deposition, the overlayer atoms occupy the sites defined by the substrate and can develop a unique orientation relationship. This phenomenon is referred to epitaxy [10]. When the thickness of the condensed material approaches a few monolayers, a new factor becomes important in the structure of the layers. The atom-atom interactions of the overlayer favor its own interparticle separation of a, while overlayer-substrate interactions favor an interparticle separation of b [10].
competition between these two quantities defines the geometrical lattice mismatch (so-called misfit);

\[ f = \frac{(b-a)}{a} \]  

(1.1)

A second parameter \( \mu \) denotes the ratio of the overgrowth-substrate atomic interaction strength to the overgrowth-overgrowth atomic interaction strength and describes the chemical bonding mismatch at the interface.

If the misfit \( f \), is small and \( \mu \), is not too small, the overlayer strains uniformly to match its lattice constant to that of the underlying substrate (commensurate state) [11]. As the misfit increases to a critical value, \( f_c \), lattice mismatching cannot be tolerated and a defect-called discommensuration-appears [10]. A discommensuration can be referred to as a semi-coherent interface, where in a narrow region atoms are out of registry with the substrate. Further increase in \( f \) decreases the mean separation of defects and a transition from the commensurate state to an incommensurate state occurs.

From the above discussion it is clear that in a system where \( f < f_c \) the first monolayer will be strained into commensurability with the substrate. Succeeding overlayers will also have a lattice matching with the layer below and be in a state of uniform strain [11]. But this process continues up to a critical thickness, \( h_c \), where it is not possible to strain overlayers into a commensurate state with the substrate. In this case the misfit is accommodated by a periodic array of misfit dislocations so that the strain is reduced in the overlayer. The misfit dislocation density increases as \( h \) increases and a coherent to incoherent transition occurs [10].
All these theories suggest that the substrate crystal can cause the overgrowth to grow with a lattice parameter that is equal to that of the substrate. Experimental observations have further shown that the substrate can cause the overgrowth to grow not only with the lattice parameter of the substrate but also with the crystal structure of the substrate rather than the normal crystal structure of the free bulk overgrowth material. This phenomenon is known as *pseudomorphism* [12].

These metastable structures can be grown in the bulk form by epitaxial growth techniques on different substrates e.g. body centered cubic (*bcc*) Cu (a = 2.87 Å) on (100) Fe (a = 2.82 Å) [13], as well as in the form of multilayers provided that the thickness of the layers is sufficiently small, typically in the nanometer or subnanometer regime e.g. face centered cubic (*fcc*) ↔ hexagonal close packed (*hcp*) transitions in Al/Ti and *bcc* ↔ *hcp* transitions Nb/Zr multilayers [2,3].

In the case of thin metallic multilayers, the description of pseudomorphic phase stabilization can be categorized in three groups based on classical thermodynamics, the effect of coherency strains, and interface-induced modulations in the stacking fault potential in close-packed structures. The following section discusses these approaches.

### 1.4. Phase stability issues in thin films

In the literature, two models have been commonly used to explain the structural stabilities in multilayers. First of these two was proposed by Bruinsma and Zangwill and considers the effect of the coherency strains. In this model a metastable structure forms as a result of the natural response of the deposit to large coherency strains induced by the
substrate and reduction of misfit in the system drives the structural transition upon decreasing the film thickness [10].

This model successfully explains why pseudomorphic transitions can occur for the case of a thin deposit on a thick substrate, with a single degree of freedom corresponding to film thickness. However, in terms of understanding phase stability in multilayers, the Al/Ti system exhibits an interesting sequence of crystal structures and interface properties, which are hard to explain through the above approach. For small equal layer thickness both metals exhibits \textit{hcp} structure and for intermediate equal thicknesses, both metals exhibits \textit{fcc} structure and at larger thicknesses both metal transforms to their bulk equilibrium \textit{fcc}/\textit{hcp} structures, respectively [20]. At first, the Ti transforms from its stable structure \textit{hcp} to a metastable structure \textit{fcc} upon increasing in thickness; and subsequently, the transition from \textit{fcc} Ti/\textit{fcc} Al to \textit{hcp} Ti/\textit{fcc} Al multilayers occurs with an accompanying decrease in misfit at the interface [17].

The second model is that due to Redfield and Zangwill (R-Z model) in which the variation in stacking fault energy with distance from metal/metal interface is considered [21]. The R-Z model proposes that the metastable structure is formed due to the stabilization of the stacking faults in a closed-packed structure. The lowering of the stacking fault potential results from the superposition of the interface-induced modulations. The R-Z model is designed only for close packed stacking sequence and does not consider the thickness ratio where this ratio is varied and different then fifty-percent [23]. It is obvious from the above discussions that none of the models is able to explain satisfactorily the various conditions observed in the phase stability of metallic multilayer systems.
1.5. A classical thermodynamic approach to phase stability in thin films

Dregia, Banerjee and Fraser have proposed a classical thermodynamic model based on the balance between the volumetric and interfacial contributions of the free energy [4]. In this model, the total energy of the system is described by a unit reference bilayer, which consists of two layers; one A layer and one B layer, and two A/B interfaces as illustrated in Figure 1.2.

The individual layer thicknesses are defined as $h_A$ and $h_B$ respectively, so that the bilayer thickness is $\lambda = h_A + h_B$. The free energy of this stable reference bilayer is;

$$G = N_A \mu_A + N_B \mu_B + 2\gamma S$$

Where $N_i$ is the number of atoms of species i, $\mu_i$ is its chemical potential, $\gamma$ is the interfacial free energy, and $S$ is the area of the interface. Interfacial area is assumed to be constant since the substrate area is fixed. Otherwise, one needs to consider the reduction in the total surface energy by the formation of equilibrium shape and minimization of the interfacial area [4]. Interfacial energy term ($\gamma$) contains both chemical and structural contributions from the nature of the bonding and also from the defect content at the interface, respectively. If we consider at least one of the components in the multilayer system has been transformed to a metastable state, we can re-define the equation (1.2) as [4]:

$$G' = N_A \mu'_A + N_B \mu'_B + 2\gamma' S$$

Where the primes refer to the new energetic conditions of the metastable phase. Since the area is fixed, both equations can be normalized for area change and therefore
Figure 1.2 A unit bilayer that defines the energetic framework of the A/B multilayer stack.
the free energy difference between Eq.1.2 and Eq.1.3 for a unit bilayer can be deduced to;

\[ \Delta g = 2 \Delta \gamma + \left[ \Delta G_A f_A + \Delta G_B f_B \right] \lambda \]  \hspace{1cm} (1.4)

Where \( \Delta g \) is normalized specific free energy of formation of the reference bilayer, \( \Delta \gamma \) is the change in the interfacial free energy, \( \Delta G_i \) is the volumetric free energy change of the reference phase metal \( i \) between the metastable and stable state and \( f_i \lambda \) is the layer thickness for metal \( i \) in the reference bilayer. Thus, equation (1.4) defines the normalized total free energy as a function of two degrees of freedom, volume fraction of layer \( i \), \( f_i \) and bilayer thickness, \( \lambda \). Note that the volume fraction of A and B can be written in terms of the other since:

\[ f_A + f_B = 1 \]  \hspace{1cm} (1.5)

Any deviation from the equilibrium phase to the pseudomorphic phase will cause an increase in the positive volumetric free energy term, \( \Delta G_i \), and must be balance with a sufficient increase in the negative interfacial free energy term, \( \Delta \gamma \), to lower the total free energy, \( \Delta g \) [4]. Therefore, \( \Delta \gamma (< 0) \) is the thermodynamic driving force for stabilization of the pseudomorphic phase. For simplicity, all the terms that scale with volume, are included in the volumetric free energy term, \( \Delta G_i \) and all terms that scale with area are included in the interfacial free energy term, \( \Delta \gamma \). The equilibrium structure in the bilayer is determined by a plot of the bilayer spacing verses total free energy change, \( \Delta g \), diagram and named as the stability diagram.

Figure 1.3 is an example of a stability diagram. Line 1 is set as the reference state where at a large bilayer thickness \( \lambda \), both layers are in their bulk stable forms; therefore, the slope of this curve is zero. Below the critical bilayer thickness \( \lambda^* \), reduction in the
interfacial energy overcomes the increase in the volumetric free energy and A transforms to A’ metastable structure with the lowest free energy and in combination with the bulk equilibrium phase of B. This case is illustrated by line 2 in Figure 1.3. From the definition of $\Delta g$, the slope of the line 2 is given as $\Delta G_A f_A$ or $\Delta G_A' (1-f_B)$ with the intersection being -2 $\Delta \gamma_{A'/B}$.

Since the interfacial free energy reduction and volumetric free energy differences are treated as fixed values, any increase in the volume fraction of A, $f_A$ must be fixed for the same bilayer spacing and a new free energy curve in $\Delta g$ verses $\lambda$ must be drawn, as illustrated in Figure 1.4. The influence of this new variation in volume fraction of A causes the slope to increase while reducing the critical bilayer thickness $\lambda^*$, for the transition to A’ [23]. The increased volume fraction (volumetric free energy contributions) reduces the bilayer length scale at which the interfacial free energy can stabilize the A’ phase.

This variation of the volume fraction and bilayer thickness in the A/B and A’/B phase stability can easily be described with the construction of a biphase diagram. It is referred to as a biphase diagram because it depicts the phase stability for a combination of two phases within the A/B multilayer stack. Figure 1.5 is an example of a biphase diagram where a phase boundary is defined by $\lambda^*$ and the slope of the boundary that separates the A/B and A’/B biphase fields is [23]:

$$m_{A'/B} = \frac{\Delta G_A}{2\Delta \gamma_{A'/B}}$$  \hspace{1cm} (1.6)
Figure 1.3 A plot of free energy, $\Delta g$ as a function of bilayer spacing, $\lambda$.

Figure 1.4 The effect of volume fraction of B, $f_B$ on the critical bilayer thickness, $\lambda^*$.
Figure 1.5 A biphase diagram representing the A/B and A`/B phase fields.
The slope, m, will always be negative ($\Delta G_A$ is ($G_{\text{metastable, } A'}-G_{\text{stable, } A}$) > 0 and $\Delta \gamma_{A'/B}$ is ($\gamma_{A'/B}-\gamma_{A/B}$) < 0, respectively). As the volume fraction of A is increased, the critical value of $\lambda^*$ at which the transition occurs increase. On the other hand, since the slope of the boundary, m is constant; the thickness of an individual A layer [=\lambda.f_A] remains constant along the boundary [23]. This agrees with the thermodynamic approach that dictates $\Delta G_A$ and $\Delta \gamma_{A'/B}$ are constant values and independent of volume fraction f and layer thickness $\lambda$.

The critical layer thickness at which the pseudomorphic transformation of stable A to metastable A' occurs can be given by:

$$h_{\text{critical}} = \frac{-2\Delta \gamma_{A'/B}}{\Delta G_A}$$

Which is also equal to the inverse of the slope of the biphase boundary, $m_{A'/B}$. In certain cases, where component B can transform to a pseudomorphic phase B', the biphase diagram exhibits a triple point. The regions of phase stability in this diagram are A/B, A/B' and A'/B as illustrated in Figure 1.6.

Similarly, the slope that separates the A/B' and A/B phase fields can be given as:

$$m_{A'/B'} = \frac{\Delta G_B}{2\Delta \gamma_{A'/B'}}$$

and the slope of the biphase boundary separating the A'/B and A/B' phase fields is given by;

$$m_{A'/B - A/B'} = \frac{\Delta G_A + \Delta G_B}{2(\Delta \gamma_{A'/B} - \Delta \gamma_{A'/B'})}$$
Figure 1.6 A biphase diagram separating the A/B, A/B' and A'/B phase stability regions.
1.6. Applications of the Biphase Diagrams

1.6.1. Al/Ti Multilayer System

In the literature, there are several studies of single film fcc Ti on different substrates [24,25]. However, Ahuja, Fraser and Banerjee et al carried out the most recent studies dealing with the structural transitions in Ti multilayers. The authors successfully applied the biphase diagram to the Al/Ti multilayer system, where at a critical value of $\lambda (=\lambda_{fcc/fcc}^*)$ the crystal structure of Ti undergoes a transition from its bulk-stable form hcp to a metastable fcc structure and subsequently at a critical bilayer thickness $\lambda (=\lambda_{hcp/hcp}^*)$ both layers transform to hcp structure [23].

In applying the model, it is assumed that due to low process temperatures (close to room temperature), the samples are kinetically constrained and effects of diffusion will be extremely localized. The second important assumption made by the authors is that the $\Delta G$’s and $\Delta \gamma$’s are constant, independent of $\lambda$ and $f$. These assumptions ignore the effect of coherency strains and state that free energy contributions of $\Delta G$’s and $\Delta \gamma$’s are only from chemical contributions. From the experimental observations, $\Delta G$’s and $\Delta \gamma$’s are deduced as $\Delta G_{Al} > \Delta G_{Ti}$ and $\Delta \gamma_{hcp/hcp} < \Delta \gamma_{fcc/fcc} < 0$, respectively. Figure 1.7 is an example biphase diagram for Ti/Al multilayer system, representing the phase stability fields as a function of inverse bilayer thickness, $1/\lambda$ and volume fraction of Ti, $f_{Ti}$.

It is obvious that the most important feature in terms of using biphase diagrams is the slope of the phase boundary which includes the thermodynamic variables, $\Delta G$’s and $\Delta \gamma$’s. The slopes of line (1), (3) and (2) are given by the equations: $-\Delta G_{Ti} / 2\Delta \gamma_{fcc/fcc}$,
Figure 1.7 The biphase diagram for the Ti/Al multilayer system [23].
\( \Delta G_{\text{Al}} / 2 \Delta \gamma_{\text{hcp/hcp}} \) and \((\Delta G_{\text{Al}} + \Delta G_{\text{Ti}} )/2(\Delta \gamma_{\text{hcp/hcp}} - \Delta \gamma_{\text{fcc/fcc}})\), respectively. Banerjee et al experimentally determined the slope of \(-\Delta G_{\text{Ti}} / \Delta \gamma_{\text{fcc/fcc}}\) by using the \( \Delta G_{\text{Ti}} \) values obtained from the literature and estimated \( \Delta \gamma_{\text{fcc/fcc}} \) to be in the range of \(-1.26\) to \(-2.76 \, \text{J/m}^2\) [23]. The absolute values of \( \Delta \gamma_{\text{fcc/fcc}} \) deduced are larger than typical values of interfacial energy of an incoherent solid/solid interface [26]. Banerjee et al argued that since the Ti results were reported by cross-sectional TEM measurements, ion milling the sample in a diffusion pumped chamber can form hydrogen-stabilized \textit{fcc}-Ti and may increase the \( \Delta G_{\text{Ti}} \) value [23].

1.6.2. Nb/Zr Multilayer System

In a similar way as discussed above, Thompson et al experimentally confirmed the stabilization of the pseudomorphic \textit{bcc} Zr and \textit{hcp} Nb in \textit{hcp} Zr /\textit{bcc} Nb multilayer system by using the classical thermodynamic model [15,16]. The biphase stability fields for Zr and Nb are shown in Figure 1.8. Unlike Zr, which undergoes an allotropic transformation from \textit{hcp} to \textit{bcc} at 1136\(^\circ\)K at 1 atm, there is no allotropic transformation observed from \textit{bcc} to \textit{hcp} for elemental Nb in the literature [16]. Using the slopes of the biphase boundaries and calculated \( \Delta G \)'s (\( \Delta G_{\text{Zr}} = 3.7 \times 10^8 \, \text{J/m}^3 \) and \( \Delta G_{\text{Nb}} = 7.5 \times 10^8 \, \text{J/m}^3 \)) from CALPHAD, the interfacial free energy differences \( \Delta \gamma_{\text{bcc/bcc}} \) and \( \Delta \gamma_{\text{hcp/hcp}} \) have been determined to be approximately \(-250 \, \text{mJ/m}^2 \) and \(-480 \, \text{mJ/m}^2 \) [15,16]. These values are on the order of semi- or incoherent solid/solid interfaces [26]. The biphase diagram shown in Figure 1.8 has been constructed using an assumption that the \( \Delta G \)'s and \( \Delta \gamma \)'s are constant, independent of \( \lambda \) and \( f \).
Figure 1.8 The biphase diagram for the Nb/Zr multilayer system [16].
1.7. Alloying

In a recent paper, a new methodology has been proposed that alloying can be used to modify the biphase stability diagrams and therefore, influence the other properties of multilayers [27]. Since the biphase boundary is simply governed by the ratio of the free energies, alloying might alter the value of $\Delta \gamma$ and/or reduce the value of $\Delta G$ [28]. In cases, where alloying addition reduces the bulk free energy of A, it might also influence the value of $\Delta \gamma_{A'/B}$. For example, the chemical contributions may vary with alloying, and the lattice parameter of the alloyed layer may also change in value, which may have implications regarding the misfit. If a positive increase in the interfacial energy change has been occurred, this would oppose the decrease in the volumetric free energy change and one would not expect to see a reduction in the critical transition layer thickness.

Considering these points a hypothetical system depicted by the biphase diagram is shown in Figure 1.9. Changes in the values of $\Delta G_A$ and $\Delta \gamma_{A'/B}$ will affect the slope of $\Delta G_A/2(\Delta \gamma_{A'/B})$ and the critical transition layer thickness might occur at larger values of $\lambda$. Another important point is that in order to maintain the thermodynamic basics, the alloy compositions used should vary in the limits of single-phase solid solution. However, deposition techniques such as sputtering are inherently non-equilibrium processes with high quench rates, which can allow the formation of supersaturated single-phase solid solutions [28].

The proposed concept has been experimentally applied to the Ti/Nb multilayer system. It is reported that in a hcp Ti / bcc Nb multilayer system, as the Ti layers reduced
Figure 1.9 Biphase diagram, showing the effect of decreasing $\Delta G_A$ and increasing $|\Delta \gamma_{A'/B}|$ on the slope of biphase boundary (3) [27].
in thickness for a fixed bilayer thickness $\lambda$, change in phase stability from $hcp$ Ti to $bcc$ Ti occurs [29]. Since the slope of the biphase boundary between $bcc$ Ti / $bcc$ Nb and $hcp$ Ti /$bcc$ Nb is equal to the $\Delta G_{Ti}/2(\Delta \gamma_{bcc/bcc})$ ratio, alloying Ti with $\beta(bcc)$ stabilizers such as V, Mo or W would result in Ti alloy layers with reduced values of $\Delta G_{Ti}$ as shown in Figure 1.10.

Although the solid solubility of V in Ti at room temperature is 2 at% and thermodynamic equilibrium composition of Ti-8%V yields a duplex $\alpha + \beta$ structure, Thompson et al successfully deposited single-phase $\alpha$-Ti-8V layers on $bcc$ Nb by sputtering Ti-8%V targets and tune the $bcc$ Ti phase stability region [28]. Since V is a $\beta$-Ti stabilizer, it should help the $hcp$ to $bcc$ phase transition in the Ti/Nb multilayers. This effect is clearly visible in Figure 1.11.

The calculated values for $\Delta G_{Ti}$ in the unalloyed and alloyed case are $3.5 \times 10^8$ and $2.5 \times 10^8$ J/m$^3$, respectively [28]. Using $\Delta G_{Ti}$ alloyed value and assuming a similar interfacial free energy reduction $\Delta \gamma$ as for Ti/Nb, predicted alloy biphase boundary has been plotted as a dashed line in Figure 1.11. The important point to be noticed is that the $\Delta G_{Ti-8V}$ actually represents a transformation from a supersaturated $hcp$ $\alpha$-Ti-8V to a $bcc$ Ti-8V, where $G_{Ti-8V}(hcp) > G_{Ti}(hcp)$. Interfacial energies $\Delta \gamma_{Ti,bcc/bcc}$ and $\Delta \gamma_{Ti-8V,bcc/bcc}$ were calculated from the slope of experimental biphase boundaries as $-265$ mJ/m$^3$ and $-570$ mJ/m$^3$. It is clear that the predicted and experimental biphase boundaries for an alloyed case agree quite significantly. These recent results suggest that controlled alloying could allow for tuning of the phase boundary to a specific volume fraction and length scale for a particular multilayer system.
Figure 1.10 Variation in $\Delta G_{Ti}$ (cal/g.atom) as function of a) V and b) Mo addition, calculated on the basis of CALPHAD [27].

Figure 1.11 Biphase diagram of Ti-8V/Nb multilayer system [28].
References


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CHAPTER 2

TECHNIQUES FOR
CHARACTERIZATION OF NANOSCALE METALLIC MULTILAYERS

2.1. Abstract

The applicability of biphase diagrams has been demonstrated for several multilayer systems. It is possible to stabilize pseudomorphic structures of different metallic layers and determine their interfacial free energy changes. There are several contributions to the $\Delta G$ and $\Delta \gamma$ terms such as; elemental intermixing (composition), alloying, structure (e.g.: coherent, semi-coherent interface), and defect density at the interfaces. These chemical and structural properties are important in determining the interfacial and bulk energy terms and must be considered for a better understanding and prediction of these nanoscale transformations.

The proposed classical thermodynamics model depends mainly on the driving force for the reduction in the interfacial energy, which is a result of the structure and chemistry of that interface [1]. The chemical component arises from the change in bonding across the interface and the structural component is due to the change in the misfit at the interface.
Another important issue is elemental intermixing. Preliminary work by Thompson et al has shown that in the case of Ti/Nb multilayer system, there is a significant amount of intermixing (~15at%Nb into Ti) [2], which is expected to influence both interfacial and bulk free energies. A thorough knowledge of various interfacial properties will assist the understanding of the driving forces that influence the phase stability in metallic multilayers.

The techniques that are used for the characterization of metallic multilayers involve high-resolution transmission electron microscopy (HRTEM) and high angle annular dark-field scanning TEM (HAADF-STEM) for imaging, 3D atom probe tomography and STEM combined with X-ray energy dispersive spectroscopy (XEDS) and electron energy loss spectroscopy (EELS) for microanalysis [3,4,5,6]. Traditionally, HRTEM has been applied for morphology, defect and crystal structure analysis of these materials. HRTEM has the great advantage of yielding local information on the atomic arrangements, projected along the direction of electron beam at a resolution comparable to the inter-atomic distance.

HAADF-STEM is another proven technique where the images are free from any delocalization effects and directly interpretable due to the incoherent nature of the imaging process [7]. In the STEM image, at high enough scattering angles (>50mrad half-angle) the intensity variations is atomic number dependent (Z-Contrast imaging) and therefore, in systems like Cu/Nb and Ti/Nb multilayers, STEM is a suitable technique to characterize the interface and also individual layer structures.

Often lateral dimensions in the nanolayered materials are around 1 to 5nm and there is a considerable need for probing the chemical and electronic information at the
nanometer scale. Material characterization at this level can be achieved with the usage of fine electron probe (~0.1nm) STEM imaging combined with XEDS and EELS analysis. The probe size, incident electron energy and the specimen thickness are primary limitations that define the achievable analytical spatial resolution in the electron microscope [8,9]. However, the factors affecting X-ray analysis such as beam broadening due to the elastic scattering events in the specimen is less pronounced for EELS [10].

One of the recent developments in TEM electron optics is the application of aberration correctors, which give a control on the spherical aberration of the microscope [11]. Major benefits of an aberration corrector are smaller and brighter (high current) probe, that yields a better spatial resolution and image contrast. The improvement in the probe characteristic can be achieved by focusing the electrons previously distributed in the tails of the probe due to the spherical aberration into the peak central maximum of the probe intensity and result is a more localized and brighter probe for both analytical and imaging purposes [12,13].

The general definition of a probe for microanalysis is somewhat different than that for imaging and it is defined as the full width tenth maximum (FWTM) of the probe intensity, which contains 90% of the electrons. Full width half maximum (FWHM) of the probe can be approximated to FWTM multiplying it by 1.8 [14]. Other limiting factors involving sample thickness, detector-sample configuration and various spectrometer parameters can be optimized to achieve the best experimental condition providing the highest spatial resolution for the microanalysis.

In the following sections, the basic principles of the characterization techniques that were used in this work are presented.
2.2. High resolution electron microscopy

2.2.1. Coherent imaging

Imaging in the transmission electron microscope arises from different contrast mechanisms. In simple conventional TEM bright field or dark field imaging, diffraction contrast or mass-thickness contrast is formed by selecting either a transmitted or diffracted beam whereas in coherent imaging (phase-contrast imaging) by using interference of many beams including the both transmitted and diffracted beams.

Mainly, coherent imaging in the transmission electron microscope relies on the fact that electrons show phase differences while they are scattered through the sample and transferred through the microscope. Considering the propagation of the electrons in the microscope, this process has two important components, first one is the specimen and the second one is the microscope.

In the microscope, the recorded total intensity $I(r)$ as an image is the convolution of a point-spread function $P(r)$ of the microscope with an exit wave function $\psi(r)$ of the object [15] and given by:

$$I(r) = |P(r) \otimes \psi_{\text{exit}}(r)|^2 \quad (2.1)$$

Where $\psi(r)$ is the electron wave function after passing through the specimen and $P(r)$ is the point spread function of the objective lens of the microscope.

2.2.1.1. Weak phase object approximation

Electrons passing regions of positive potential, i.e. atomic nuclei, change phase by an amount proportional to the potential at the scattering site [16]. When the electrons are scattered only once (phase change $-\pi/2$) on their way through the specimen, the specimen
acts as a weak phase object (WPO). For larger phase changes, where multiple scattering events occur, the specimen is defined as a strong phase object [16].

Weak phase approximation is valid only for very thin samples (< 20 Å thickness) and the image contrast is directly related to the projected potential of the object. Neglecting dynamical scattering (WPO), the exit-wave, which is modulated in phase, can be written in real space as:

$$\psi_{\text{exit}}(r) \sim \exp\left[i\sigma \nu(r)\right] \sim 1 + i\sigma \nu(r) + \ldots$$  \hspace{1cm} (2.2)

Where $\sigma$ is a scaling factor and $\nu(r)$ is the projected atomic potential of the specimen.

In Real space intensity is given by:

$$I(r) = \left[1 + i\sigma \nu(r) + Z(\nu^2)\right] \otimes P(r)$$  \hspace{1cm} (2.3)

Where $Z(\nu^2)$ is the third order term in the power series and the intensity is given by:

$$I(r) \approx 1 + 2\sigma \nu(r) \otimes P_{\text{WPO}}(r)$$  \hspace{1cm} (2.4)

Where $P_{\text{WPO}}(r)$ is the point spread function in the weak phase approximation.

So the image intensity in Fourier space for a weak phase object is:

$$I(k) = \delta(k) + 2\sigma V(k) \sin \chi(k)$$  \hspace{1cm} (2.5)

Thus image intensity of the $k^{\text{th}}$ frequency is proportional to $V(k)$ (the $k^{\text{th}}$ Fourier coefficient of the projected potential) and to the $\sin \chi(k)$ oscillation [16].
2.2.1.2. The microscope

The interaction of the electron beam with the specimen forms the information on
the spatial distribution of specimen potential and the microscope transfers this
information from specimen exit-surface wave to the image intensity. In the case of a
WPO, without any objective lens aberrations a focused electron image would show zero
contrast. The role of a microscope here is to bring the transmitted and diffracted waves in
phase or out of phase by introducing a phase shift that provides the amplitude contrast
(intensity)[16]. The amount of phase shift necessary to form this contrast is set by the
defocus of the microscope (where $C_s$ is fixed). According to Scherzer the relation
between the defocus and the phase shift is given by:

$$\chi(k) = \frac{1}{4} C_s \lambda k^4 + \frac{1}{2} \Delta f \lambda k^2$$

(2.6)

Where $C_s$ is the spherical aberration, $\lambda$ electron wavelength, $k$ reciprocal spatial
frequency and $\Delta f$ defocus. Defocus value for the widest range of $k$ where the function
$\sin \chi$ is close to unity and has the same sign is described as the Scherzer defocus [17] and
is given by:

$$\Delta f = -1.2 \sqrt{C_s \lambda}$$

(2.7)

This condition is the Scherzer resolution and for a thin specimen, the image can
be approximately interpreted in terms of its projected potential. Scherzer resolution (point
resolution) is given by:

$$d_p = 0.66 C_s^{1/4} \lambda^{3/4}$$

(2.8)

Point resolution of the microscope is fixed depending on its objective lens
spherical aberration coefficient and electron-wave length. Beyond the Scherzer (or point)
resolution, high spatial frequency information is partially transferred but cannot be directly interpretable and at far enough spatial frequencies the signal finally diminishes to zero. This zero point is the information limit of the microscope. Besides the spherical aberration and electron wavelength of the microscope, which defines the point resolution of the microscope, there are other factors determine the imaging and the information transfer in the microscope such as the illumination, chromatic aberration and the instabilities in the microscope. All these factors impose constraints as damping envelope functions and the imaging deviates from an ideal coherence condition to a partial coherence condition.

The temporal coherence \((E_T)\) damping envelope function imposes the chromatic aberration, the energy spread of the electron source and the instabilities of the objective lens current [18], as below:

\[
E_T = \exp\left(-\frac{1}{2} \pi^2 \lambda^2 \Delta^2 k^4\right)
\]  

(2.9)

Where \(\Delta\) is the defocus spread and given by:

\[
\Delta = C_c \sqrt{4 \left(\frac{\delta I}{I}\right)^2 + \left(\frac{\delta E}{V}\right)^2}
\]

(2.10)

Where \(V\) is the accelerating voltage of the electrons, \(\delta I/I\) is objective lens current instability; \(C_c\) is the chromatic aberration coefficient for the objective lens and \(\delta E\) is the energy spread of the electron source.

The information limit due to the chromatic aberration is equal to:

\[
d_i = \sqrt{\frac{\pi \Delta \lambda}{2}}
\]

(2.11)
Spatial coherence is the spatial coherence of the illuminating beam, which is the convergence angle $\alpha$, in combination with defocus $\Delta f$ and spherical aberration of the objective lens $C_s$ [19], as below:

$$E_s = \exp\left[-2\pi^2\alpha^2k^2(C_s\lambda^2k^2 + \Delta f)^2\right]$$  \hspace{1cm} (2.12)

So the spatial coherence is related to the brightness of the illuminating beam. For Field Emission Guns (FEG), the high brightness of the gun results an incidence angle of ~0.1mrad [19]. The partial coherence defines the information limit by damping the higher frequency oscillations in the contrast transfer function of the microscope and further improvement in the coherence will push the information limit of the microscope. Figure 2.1.a is the Young's fringe image, from gold particles on amorphous carbon film sample, showing the sub Angstrom (0.07nm) information limit achieved due to the improvements in the stability of the uncorrected TITAN S/TEM 80-300 microscope at OSU and Figure 2.1.b is the microscope contrast transfer function at Scherzer imaging condition (defocus of 56nm ($\Delta f$), 300kV accelerating voltage, ~4nm defocus spread ($\Delta$) and 0.1mrad beam convergence angle ($\alpha$)) representing the 0.2nm point resolution and damping effects of the envelope functions on the microscope transfer function.

### 2.2.2. Incoherent imaging

As explained in coherent imaging process, image contrast can be formed using coherence interference of the many scattered beams including the transmitted and diffracted beams. This imaging process brings the advantage of high signal to noise ratio combined with sub-Angstrom information limit (~0.07nm) capability. However, due to
Figure 2.1 (a) Young’s fringe image of the gold particles on carbon film sample showing the sub-Angstrom information limit (b) Microscope contrast transfer function at Scherzer imaging condition displaying the point resolution ($d_p$) and damping effects of the envelope functions.
the strong and complicated interference effects the results from coherent imaging are not
directly interpretable and need further image processing and simulation steps to
reconstruct the full information transferred through the microscope. Spherical aberration
and defocus in HRTEM also result in the delocalization of the image details at the
interfaces and grain boundaries and has to be corrected using image simulation methods.

Lord Rayleigh is the first pioneer of the incoherent imaging and he showed that
when an object is illuminated by a source over a wide range of angles (due to the
reciprocity this is analogous to a large angular range of the detector area in STEM) the
coherence interference effects are destroyed and the object can be treated as self-
luminous [15]. In such case, the intensity in real space becomes a simple convolution of
the intensity of the probe wave function (or point spread function of the probe forming
lens: which is the intensity distribution in the probe), P(r) and specimen or object
function O(r) (which is the specimen information) [15].

For very thin specimen we can write the incoherent image intensity as:

\[ I(r) = |P(r)|^2 \otimes O(r) \]  \hspace{1cm} (2.13)

and,

\[ O(r) = |\psi(r)|^2 \] \hspace{1cm} (2.14)

Where \( \psi(r) \) is the exit-wave function.

This simple nature of the incoherent imaging leads to the direct interpretation of
the atomic resolution images without any phase problem whereas the direct convolution
of the exit wave function and the point spread function of the microscope results in
complex amplitude during the coherent imaging process.
In the following sections the formation of incoherence in the STEM image is divided into two directions with respect to the incident electron beam in the microscope; intercolumn incoherence; the incoherence between the atomic columns perpendicular to the electron beam direction and intracolumn incoherence, the incoherence in the atomic columns towards the electron beam direction.

2.2.2.1. Intercolumn incoherence

In incoherent STEM imaging, intercolumn incoherence can be explained by the combinational effect of two concepts, (a) thermal diffuse scattering (TDS) which becomes important as the electron scatters at high angles and (b) the block state filtering action of the ADF detector which explains the incoherency even if we include the zero-order Laue zone (ZOLZ) discs for image formation (where the TDS does not play a dominant factor)[15,20,21,22,23]. The general STEM probe wave function is given by:

\[ P(r) = \int A(k) e^{i\chi(k)} e^{i(k \cdot r)} dk \]  \hspace{1cm} (2.15)

Where \( r \) and \( k \) are the two-dimensional position vectors in real and reciprocal space, respectively, \( A(k) \) is the aperture function (which is one inside the aperture and zero outside) and \( \chi(k) \) is the phase shift. The phase shift is given by:

\[ \chi(k) = \frac{\pi}{2} C_s \lambda^3 k^4 + \pi \Delta f \lambda k^2 \]  \hspace{1cm} (2.16)

Where \( C_s \) is the spherical aberration and \( \Delta f \) is the defocus of the microscope.

Assuming a very thin specimen (pure phase object) the specimen function can be written as;

\[ O(r) = \left( \frac{\pi}{\lambda U} \right)^2 |W(r) \otimes D(r)|^2 \]  \hspace{1cm} (2.17)
Where, $V(r)$ is the projected potential, $D(r)$ is detector function and $U$ is the accelerating voltage.

By using equation (2.15) we can plot the probe intensity distribution depending on the important microscope parameters: defocus $\Delta f$, spherical aberration coefficient $C_s$, electron wavelength $\lambda$, and probe convergence angle $\alpha$. The simple specimen function in equation (2.17) is derived under the assumption of a thin specimen. However, Nellist and Pennycook used a theory of dynamical scattering with no absorption effects where they considered the thickness of the specimen under the electron beam probe [21,22].

In this Bloch wave formulation of dynamical scattering, the ADF intensity (in reciprocal space) for the case of scattering from a stationary lattice of thickness $z$, is given by:

$$I(Q,z) = \sum_{g} D_g \left[ A(k) A^*(k + Q) x \sum_{j,k} \Phi_{0}^{(j)}(k) \Phi_{0}^{(k)}(k) \Phi_{g}^{(j)}(k) \Phi_{g}^{(k)}(k) \right] dk$$

$$x \exp \left[ -i2\pi(l_z^{(j)}(k) - l_z^{(k)}(k)) \right]$$

(2.18)

Where $Q$ is the image spatial frequency, $\Phi_{g}^{(j)}(k)$ is the $g$ Fourier component of the $j^{th}$ Bloch wave solution, whose eigen value gives a longitudinal component of wave vector of $l_z(k)$ and $D_g$ is the detector function.

The partial plane-waves $k$ and $k+Q$ as illustrated in Figure 2.2 excite a set of Bloch states represented by the sum over $j$ and $k$ and interference can occur scattering into the same Bragg beam $g$ where the discs overlap. At this point the wave function is
Figure 2.2 The electron scattering geometry in STEM [21].
the sum of many Bloch states propagating at different rates in the crystal and interfering constructively or destructively. The image intensity will be integrated and averaged out by the detector over the many overlapping discs forming the image contrast and thus if the discs are not overlapping there will be no contrast. At this point the effect of detector on the summation over the Bragg beams can be described using two parameters, the detector function \( D_g \), and the Fourier components of the Bloch states, \( \Phi_g^{(i)}(k) \) and \( \Phi_g^{(k)*}(k) \). And we can write a quantity \( C_{jk} \):

\[
C_{jk}(k) = \sum_g D_g \Phi_g^{(i)}(k)\Phi_g^{(k)*}(k)
\]  

(2.19)

In practice, this filtering factor, \( C_{jk}(k) \) describes the contribution of each Bloch states to the ADF image intensity and it dictates how strong any individual state contributes to the Z-contrast image [21,22]. For instance, highly localized 1s-type Bloch states will have larger high-angle Fourier components and thus contribute more to the \( C_{jk}(k) \) term [22]. Due to this highly localized nature of the 1-s states when the probe scans over specimen area each atomic column acts as an independent scatterer providing the intercolumn incoherence. The resulting image intensity can be described as the convolution of the probe intensity with the 1s states in the object.

The second approach, i.e. the thermal diffuse scattering, considers the vibrating atoms as an independent generator of diffuse scattering, which breaks the intercolumn coherence. Figure 2.3 represents the total, elastic and thermal diffuse scattering contributions to the ADF STEM image with the scattering angle. For high angle detectors the angular range is 1-2 (75-150mrad)[23].
Figure 2.3 Total, elastic and thermal diffuse scattering (TDS) from an isolated Si atom at room temperature per unit solid angle [23].
2.2.2.2. Intracolumn incoherence

As explained above, the intercolumn incoherence mainly originates from the detector geometry with additional loss due to diffuse scattering. However, the detector geometry by itself is not enough to break the coherence of the scattering along the atomic columns. The intensity summation in the reciprocal space becomes inefficient due to the flat shape of the Ewald sphere ($R_{\text{Ewald sphere}}=1/\lambda$), which cuts the reciprocal lattice points at certain wavelengths used in the electron microscope [20]. Therefore additional incoherence may be required to reduce the intracolumn coherence by the thermal vibrations of the atoms through phonon scattering. Phonon scattering will disturb the coherence in the column to some extent since the typical momentum of phonons is less than the reciprocal lattice spacing. There will be partial coherency along the columns in the direction parallel to the electron beam.

In this sense one can describe the atomic column as independent packets of atoms in which the atoms contained within a packet are partially coherent and the number of atoms in this packet depends on both the detector inner-angle and the Debye-Waller factor, but is independent of atom spacing along the column [20]. The atomic number dependency $Z$, for Rutherford elastic scattering scales as $Z^2$ but the atomic electron cloud screens the coulomb potential of the nucleus and $Z$-dependence for screened Rutherford scattering deviates from this number and becomes approximately $Z^{3/2}$.

2.2.3. Practical aspects of incoherent STEM imaging

In order to provide the proper imaging conditions in the STEM, the electron probe has to be optimized for the resolution and the contrast in the microscope. In conjunction with Rayleigh’s resolution criteria for two point scatters we can write the STEM
resolution limit as:

\[ d_r = \frac{0.61\lambda}{\alpha_{opt}} = 0.43C_s^{1/4}\lambda^{3/4} \]  \hspace{1cm} (2.20)

So the resolution in STEM (at fixed accelerating voltage) is either diffraction limited, which is the size of illumination aperture or aberration limited, which is the spherical aberration of the electron microscope. As mentioned before the probe intensity is convoluted with the object intensity. So the structure of the probe (size and shape) will determine the resolution and the image contrast achieved in the microscope. Resolution is physically proportional to the full width half maximum (FWHM) of the probe intensity profile and the image contrast depends on the probe shape such as the probe tails and height (intensity). In order to achieve the best imaging condition in a microscope where the aberrations are not corrected, the convergence angle and defocus must be set such that an electron probe with a narrow FWHM and minimum probe tails can be obtained. This optimum STEM imaging condition is named as Scherzer incoherent imaging condition and given by:

\[ \alpha_{opt} = \left( \frac{4\lambda}{C_s} \right)^{1/4} \]  \hspace{1cm} (2.21)

\[ \Delta f_{opt} = -(C_s\lambda)^{1/2} \]  \hspace{1cm} (2.22)

Where \( \alpha_{opt} \) is the optimum convergence angle (in mrad) and \( \Delta f_{opt} \) is the optimum defocus (in nm). The calculated Scherzer optimum conditions for an uncorrected 300kV FEI TITAN S/TEM microscope with a \( C_s \) of 1.2mm are 9mrad convergence angle and –48nm defocus value. Figure 2.4 shows the calculated probe point spread function (PSF) using
Figure 2.4 (a) Probe point spread function (semi-probe intensity profile) and (b) STEM microscope contrast transfer (MTF) function for an uncorrected 300kV FEI TITAN S/TEM microscope at the Scherzer optimum condition.
equation (2.15) and the corresponding microscope transfer function (MTF) for the Scherzer optimum condition of an uncorrected 300kV FEI TITAN S/TEM transmission electron microscope. In the absence of instabilities the theoretically achievable probe size was predicted to be 0.07nm. The STEM resolution limit achieved using this microscope was 0.136nm, which is the lattice spacing of \{400\} planes in Si \textlangle 110\rangle crystal direction and known as the Si dumbbells shown in Figure 2.5 (a).

In practical applications, incoherent Z-contrast STEM imaging requires an inner detector semi-angle at least three times larger than the convergence angle (collection semi-angle > 40mrad) and a detector angular width of about 50mrad [24]. Figure 2.6 shows the measured HAADF collection semi-angles as a function of camera length for an uncorrected 300kV FEI TITAN S/TEM microscope and corrected 300kV FEI TITAN S/TEM microscope. The camera length values for practical usage were selected considering an optimum signal to noise ratio. Thus, a collection semi-angle range of 51-335mrad (at 120mm camera length) for the uncorrected microscope and 46-325mrad (at 91mm camera length) for the corrected microscope was used in HAADF STEM imaging of all samples in this work.

2.3. Aberration correction in STEM

The resolution in STEM mainly depends on the spherical aberration coefficient of the probe-forming lens, \(C_s\) and the wavelength of the electrons, \(\lambda\). One can always increase the accelerating voltage of the microscope up to a point where it does not cause any radiation damage and reduce the wavelength of the electrons. The knock-on energy threshold for atomic displacement of most materials is below 300kV. The other feasible option of improving resolution is the correction of the third order spherical aberration (\(C_3\)
Figure 2.5 (a) uncorrected HAADF STEM image of Si <110> dumbbells and (b) Fast Fourier transform (FFT) of the image showing the \{400\} spatial frequency.
Figure 2.6 The HAADF collection semi-angles vs. camera length of (a) an uncorrected 300kV FEI TITAN S/TEM microscope and (b) a probe corrected 300kV FEI TITAN S/TEM microscope.
or \( C_\perp \) of the probe-forming lens. As described by Scherzer, in rotationally symmetric electromagnetic fields, the outer zones of the lenses focus the electrons always more strongly than the inner zones, therefore electrons, which enter the focusing lens further away from the optical axis are focused at a different point than the electron closer to the optical axis [24]. This lens action is the reason behind the spherical aberration and causes blurring of the image and consecutive loss of the resolution in the microscope. However, aberration correctors offer a control on the spherical aberration of the microscope and one of the common types of them is the hexapole corrector. The basic principle of a hexapole corrector is to create a negative spherical aberration using a non-round lens and then compensate the positive spherical aberration of the probe forming round lens [24,25]. Figure 2.7 shows a schematic of a hexapole corrector, which consists of two non-round hexapole lenses (H) and two round transfer doublet lenses (TL). Hexapoles, without affecting the paraxial rays (inner rays/red), locate the third order deviations (outer rays/green) on a diverging cone and thus introduce negative third order spherical aberration that compensate the positive spherical aberration of the probe-forming lens.

The benefits of aberration correction are a finer and brighter probe, yielding a better spatial resolution and image contrast. Since the image intensity in STEM is the convolution of the probe intensity with the object function of the specimen, simply reducing the Full Width Half Maximum (FWHM) and increasing the peak height of the probe intensity improves the spatial resolution and also signal-to-noise ratio in the microscope [26,27,28]. This can be achieved by focusing the electrons that are previously distributed in the tails of the probe due to the spherical aberration into the peak central maximum of the probe intensity.
Figure 2.7 Ray diagram showing the divergence action of the hexapole corrector [25].
After correction, the probe is no longer spherical aberration (C₃) limited so we can open up the limiting aperture for the probe and use larger convergence angle values (α_opt is increased). Practically, this means we can put more current into the source at a given resolution and improve not only the contrast but also the analytical signal. The electron beam current in the electron microscope is given by:

\[ I = \beta \cdot \pi \left( \frac{d_o}{2} \right)^2 \pi \alpha^2 \]  

Where \( \beta \) is the brightness of the gun (5x10⁸ A/cm²sr for FEG), \( \alpha \) is the convergence angle and \( d_o \) is the source size. Table 1.1 lists the calculated and measured beam current values in pA for an uncorrected 300kV FEI TITAN S/TEM and probe corrected 300kV FEI TITAN S/TEM at different convergence angles and probe sizes. As seen in the Table 1.1, at a probe size of 0.12nm, the corrected microscope has about four times more electron beam current than that of an uncorrected microscope. At large angles it is also important to consider the possible effects of the spherical aberrations on the probe shape. The minimum intensity in the probe tails is important for both analytical and imaging purposes at atomic scale. It is essential to minimize the cross talk between the atomic columns by reducing the tail intensity and thus localize the probe intensity to the atomic columns. The phase shift caused by the axial aberration up to C₅ (fifth order spherical aberration) can be written as:

\[ \chi(\omega) = \text{Re} \left[ \frac{1}{2} \omega^2 A_1 + \frac{1}{2} \omega^2 C_1 + \frac{1}{3} \omega^3 A_2 + \omega^2 A_2 + \frac{1}{4} \omega^4 A_3 + \frac{1}{4} (\omega \sigma)^2 C_3 \right] \\
+ \omega^3 \sigma S_3 + \frac{1}{5} \omega^5 A_4 + \omega^3 \sigma^2 B_4 + \omega^4 \sigma D_4 + \frac{1}{6} \omega^6 A_5 + \frac{1}{6} (\omega \sigma)^3 C_5 \]
<table>
<thead>
<tr>
<th>Probe size d (nm)</th>
<th>Measured current I (pA)</th>
<th>Calculated current I (pA)</th>
<th>Convergence angle $\alpha$ (mrad)</th>
<th>Aberrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>10</td>
<td>12</td>
<td>9</td>
<td>uncorrected</td>
</tr>
<tr>
<td>0.12</td>
<td>39</td>
<td>47</td>
<td>18</td>
<td>corrected</td>
</tr>
<tr>
<td>0.1</td>
<td>70</td>
<td>74</td>
<td>25</td>
<td>corrected</td>
</tr>
</tbody>
</table>

Table 2.1 Calculated and measured beam current values for an uncorrected 300kV FEI TITAN S/TEM 80-300 and probe corrected 300kV FEI TITAN S/TEM at different convergence angles and probe sizes.
\[ + \omega^4 \sigma^2 S_5 + \omega^5 \sigma D_5 + \ldots \]  \hspace{1cm} (2.24)

Where, the complex coordinates in the aperture plane are
\[ \omega = \alpha + i \beta \]  \hspace{1cm} (2.25)

The existing CEOS hexapole probe corrector at OSU can correct the aberrations up to third order and measure them up to fifth order. Table 1.2 shows the terminology of these aberrations and subsequently Table 1.3 indicates the upper limits in order to achieve 0.08nm STEM resolution using a probe corrected 300kV FEI TITAN S/TEM microscope.

As mentioned previously STEM image is a convolution of the probe intensity with the object function. Therefore, in order to determine the existing aberrations one needs to extract the probe intensity information from a STEM image. We can digitize these aberrations eventually by processing the under and over focused probe images which contains the characteristics of the aberrations oweing to their symmetries [29]. If we define the specimen information as \( f(x,y) \) and probe intensity as \( g(x,y) \), the image intensity \( h(x,y) \) in Fourier space can be written as:
\[
H(X,Y) = F(X,Y)G(X,Y)
\]  \hspace{1cm} (2.26)

Where \( F, G \) and \( H \) indicate the Fourier transforms of \( f, g \) and \( h \), respectively. If we approximate a Gaussian function for a focused probe \( (G_1) \), the probe intensity of defocused probe can be extracted from one focused \( (h_1) \) and one defocused image \( (h_2) \) [29]:
\[
G_2 = G_1 \frac{H_2}{H_1}
\]  \hspace{1cm} (2.27)
Table 2.2 Terminology of the aberration coefficients up to 5th order.

<table>
<thead>
<tr>
<th>Order n</th>
<th>Name</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Defocus</td>
<td>C₁</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order spherical aberration</td>
<td>C₃</td>
<td>C₅</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order axial coma</td>
<td>B₂</td>
<td>B₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order star aberration</td>
<td>S₂</td>
<td>S₅</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order three-lobe aberration</td>
<td></td>
<td></td>
<td>D₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order rosette aberration</td>
<td></td>
<td></td>
<td></td>
<td>R₅</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ν (ν=n+1) fold axial astigmatism</td>
<td>A₁</td>
<td>A₃</td>
<td>A₃</td>
<td>A₄</td>
<td>A₅</td>
</tr>
</tbody>
</table>

Adjustable

**Factory aligned**

Except S₅ and R₅ all aberrations measured up to 5<sup>th</sup> order

Table 2.3 Tolerable aberration coefficients up to 5<sup>th</sup> order to achieve 0.08nm STEM resolution at 24mrad beam convergence angle.

<table>
<thead>
<tr>
<th>Order n</th>
<th>Name</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Defocus</td>
<td>0.8nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order spherical aberration</td>
<td>2μm</td>
<td>8.4mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order axial coma</td>
<td>14nm</td>
<td>16.5μm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order star aberration</td>
<td>0.5μm</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order three-lobe aberration</td>
<td></td>
<td>16.5μm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n&lt;sup&gt;th&lt;/sup&gt; order rosette aberration</td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ν (ν=n+1) fold axial astigmatism</td>
<td>0.8nm</td>
<td>41nm</td>
<td>2μm</td>
<td>89μm</td>
<td>234μm</td>
</tr>
</tbody>
</table>
After successful extraction of the probe images (intensity) the aberrations can be digitized by taking n line profiles across the probe images at a constant angular step and then considering the width, asymmetry and curvature of these profiles [29].

2.4. Atom probe tomography (APT)

Atom probe tomography (APT) is an evolving high spatial resolution technique for the characterization of nanomaterials. An important application of APT is the tomography feature that enables construction of 3D composition distribution of the materials at near-atomic resolution.

One of the common difficulties encountered in APT is the field evaporation artifacts created due to difference in the evaporation rates of the probed elements. Peak overlap in the mass charge ratio spectrum of the elements is another challenge that needs to be carefully addressed in order to extract accurate 3D composition profiles.

As previously explained the phase stability in nanoscale multiayers depends on the competition between the volumetric free energies and the interfacial energies of the components. Volumetric free energies can be affected by compositional variations resulting in remarkable differences in the phase stability of these materials. Preliminary work by Thompson et al has shown that in the case of Nb/Ti multilayers, there is a significant amount of intermixing (~15at% Nb into bcc Ti), which is expected to influence interfacial and bulk free energies [2]. Knowledge of compositional variations will assist in developing and understanding the driving forces that influence the phase stability in metallic multilayers.
The basic principle of atom probe is dc voltage pulsing onto a very fine sharp tip that has a radius of curvature of ~50nm. Smaller the curvature is more the electric field that can be applied onto the tip. The electric field $F$ at the tip is given by;

$$ F = \frac{V}{kr} $$

(2.28)

Where $V$ is the voltage, $r$ is the tip curvature and $k$ is a constant. The electric field causes the field evaporation at the tip and in order to maintain the evaporation as the tip radius decreases, the electric field must be gradually increased typically from 5kV to 15kV. The theory of field evaporation is based on field desorption; the removal of adsorbed species from the surface [30]. The ionic states of surface atoms are generally metastable. In the presence of an electric field, these ionic states become more stable as the distance from the specimen surface increases. At some point it is possible to remove an ion by overcoming a reduced thermal energy barrier [30]. The field-evaporated atoms are spatially resolved in x and y directions using a position sensitive detector and the depth, $z$ is determined from the sequence of the evaporated atoms. Thus it is possible to construct a 3-D distribution of the atoms analyzed. The microanalysis of the atomic species are done by using a time of flight spectrometer which scales the isotopes of the atoms according to their mass to charge ratio and their intensity over a spectrum [30].

2.4.1. Atom probe sample preparation

The different stages of the atom probe sample preparation of multilayered thin films are illustrated in Figure 2.8. The initial pillars have a flat top as shown in Figure 2.8 (a) and layers are deposited on these flat top 2μm diameter Si pillars as shown in Figure
2.8 (b). The multilayered film is designed such that flashing is minimum (the sudden removal of the film from the tip surface during the field evaporation due to the poor adhesion of the film to the substrate). To improve the adhesion of the film to the Si substrate, ~100nm thick Ti layer was first deposited and this intermediate layer followed by deposition of 100 bilayers of Cu/Nb multilayers at layer thickness of 3nm Cu and 5.5nm Nb. The final 200nm thick Cu protective layer on top is deposited as a buffer layer to reduce the Ga ion damage during the FIB milling.

In order to give the necessary curvature of ~50nm for field evaporation, the pillars were sharpened at 30kV and 5kV, respectively, using a Ga ion source in the FIB as shown in Figure 2.8 (c). All the samples were characterized using an Imago™ Local Electrode Atom Probe located at the University of North Texas.

2.5. Electron energy-loss spectroscopy (EELS)

In conventional TEM, the imaging process is based on the contrast arising from the interference of the elastically scattered electrons. The incident electrons can also undergo elemental specific inelastic scattering events that are used in various spectroscopy techniques such as in EELS. In EELS, the incident electron beam passes through the TEM specimen and reaches to the EELS spectrometer. The spectrometer disperse these inelastically scattered electrons such that all those entering with same energy-loss, E relative to the their initial zero loss energy state, E₀, are focused to the same point on the dispersion plane of the spectrometer. The spectrometer acts somewhat like a glass prism that disperses the white light. The intensity as a function of
Figure 2.8 Atom probe sample preparation steps for multilayered thin films (a) Flat top pillars (b) Deposited film on a flat top tip and (c) Annular milling of the tip.
the energy-loss is detected by the spectrometer up to an angular cone range. Therefore, the collection angle $\beta$ is one of the most important parameters that defines the angular range of the collected signal and consequently the efficiency of the collection in the spectrometer.

The first characteristic peak in the EELS spectrum is the zero-loss signal, which represents the unscattered electrons, elastically scattered electrons and phonon excitations. The second visible feature, in the low loss part of the EELS spectrum (\(<40-50\text{eV}\)) are the plasmon excitations which occur due to inelastic interaction of electron beam with the weakly bonded outer shell valance electrons. And the last characteristic peak is the core-loss edge (\(>50\text{eV}\)) caused by inelastic interactions with inner shell excitations. This ionization edge signal is superimposed onto the background created by the valence shell excitations.

In EELS, this particular core level energy loss is proportional to the “energy differential cross section”, which is the probability of an incident electron that can scatter within the appropriate angular range while losing energy loss $E$ \([10,31,32]\).

Thus, the intensity of the core edge, $I_{\text{core}}$ is given by:

$$ I_{\text{core}}(\beta\Delta) = I_o(\beta\Delta)N\sigma(\beta\Delta) \quad (2.29) $$

Where $I_o$ is the incident electron beam intensity at a scattering angle $\beta$ (mrad) and energy loss range $\Delta$ (eV), $N$ is the number of atoms per unit area participating in the scattering event and $\sigma(\beta\Delta)$ is the part of the total cross section (partial cross section) at a scattering angle $\beta$ and energy loss range $\Delta$.

In this expression a partial cross section rather then a total cross section is considered for a particular range of collection angles and energy window. If we
determine the partial cross section, it is possible to drive N from the ratio of $I_{\text{core}}/ I_o$ in the EELS spectrum and get quantitative information regarding the specimen composition [31,32].

Another important characteristic in the core-loss edge signal is the “near edge structure” imposed on the core loss intensity. The exited electron due to the inelastic scattering may not have the enough energy to escape to vacuum and may reside in one of the unoccupied energy levels above the Fermi energy $E_F$ [31]. The intensity oscillations above the $E_c$ of the particular core edge reflect the density of states and reveals useful information regarding the bonding of the material. In addition to this, changes in the binding energy relative to its value in the pure (solid) state, reflects its character as an ionization threshold shift in the EELS spectrum and is widely referred as a chemical shift [31,32].

2.6. X-ray energy dispersive spectroscopy (XEDS)

As described above the incident electrons can have inelastic interactions with the inner shell electrons and lose characteristic energies. When the inner shell electron receives the energy greater than its binding energy from the incident electron beam, it can also make an upward transition to an unoccupied energy state above the Fermi level leaving the atom excited (or ionized). Following this event a de-excitation process occurs and an outer shell electron (or an inner-shell electron of lower binding energy) fills the core hole resulting in an excess energy in the form of electromagnetic radiation (X-rays) [31,32]. In XEDS this characteristic signal is collected for microanalysis of the material imaged under the incident electron beam and the detected X-ray signal intensity is given
by [32]:

\[ I = I_o N \sigma \omega \varepsilon \]  \hspace{1cm} (2.30)

Where \( I_o \) is incident electrons flux, \( N \) is the number of atoms per unit area in the volume examined, \( \sigma \) is the X-ray ionization cross-section, \( \omega \) is the fluorescent yield, and \( \varepsilon \) is the collection efficiency of the X-ray detector.

**2.7. Analytical electron microscopy (AEM)**

In STEM imaging, a fine (~0.1nm) converged electron beam (\( \alpha_1 \)) is continually scanned over the sample area resulting a stationary convergent beam electron diffraction (CBED) pattern of each scanned position at the HAADF detector plane. As seen in Figure 2.9 the high angle annular dark field (HAADF) detector collects all the electrons scattered to high angles (\( \beta_2/46-325\text{mrad} \)) and forms the STEM image contrast, which is atomic number dependent. When the scanned electron beam (probe) size is on the order of or smaller than the lattice spacing of the material, it is also possible to resolve the atomic columns and conduct lattice imaging.

This high spatial resolution imaging technique is often combined with EELS (\( \beta_1 \)) and XEDS (\( \beta_3 \)) techniques and becomes a powerful analytical tool enabling chemical and structural characterization of the material at sub nanometer or even atomic level. Therefore it is possible to gather simultaneous high spatial resolution structure and chemical information from the sample of interest in the analytical electron microscope. The important characteristic signals and their critical angular scattering range are demonstrated for the analysis of an A/B multilayer in Figure 2.9.
Figure 2.9 Analytical electron microscope (AEM).

- $\alpha_1$: 18-25 mrad
- $\alpha_2$: 20° (+10° tilt)
- $\beta_1$: 20 mrad
- $\beta_2$: 46-325 mrad
- $\beta_3$: 0.13 sr

XEDS (-z, -y)

Profile direction / $\alpha_2$ -tilt axis

HAADF

EELS aperture

EELS
2.8. Sample preparation for high resolution electron microscopy

Despite the significant advances in the transmission electron microscopy: such as applications of aberration correction and monochromation, sample preparation is still one of the most critical steps determining the quality, and precision of the results. The important challenge here is to prepare samples that are thin enough for electron transparency (<100nm for conventional TEM, <10nm for HRTEM), free from any surface damage and have negligible surface roughness. The presence of any surface artifact would make both the interpretation of the image and the chemical analysis difficult or impossible. In general surface artifacts (surface amorphization, surface roughness or oxidation) limit the resolution of the imaging and the chemical analysis employed in high-resolution electron microscopy (HREM) and analytical electron microscopy.

Other important concerns regarding the specimen are the thickness where thicker samples often induces dynamical scattering effects in HRTEM (strong phase object), column to column interactions in Z-contrast STEM imaging and plural inelastic scattering events in EELS.

2.8.1. Low energy ion milling

The conventional broad Ar ion beam milling and Ga focused ion beam (FIB) milling are two widely used techniques both enabling TEM samples to be prepared in plan-view and cross-section, and from specific, sub-micron semiconductor devices. However, bombarding a specimen with these energetic ions or neutral atoms may cause a well-known artifact, i.e. surface damage or surface amorphization [33,34].
characteristic amorphization layer is important especially for metallic crystalline materials since they are easily beam damaged due to their low cohesive energies (Al 3.5eV) [35]. Usual FIB Ga ion beam milling with an accelerating voltage of 30kV causes surface damage about 30nm thickness and even the lower energy end-finish with a 5-10kV focused Ga beam leaves a damage layer of 5-10nm thickness [36,37]. Figure 2.10 displays the change in the amorphous layer thickness of single crystal Si with Ga ion energy. It is clear that decreasing the milling voltage reduces the thickness of the FIB amorphisation damage. Likewise in Ga milling, the conventional Ar broad beam milling at high ion energies results in a surface damage layer at comparable thickness to FIB milling as seen in Figure 2.11 [38].

The quality of the TEM samples can be improved by the application of low energy (<2000V) and low angle (0-15°) milling practices [33,34,39].

2.8.2. Low energy focused Argon ion milling (Nanomill™)

Focused Ar ion beam milling is a recently developed technique, which applies a focused low energy (50-2000V) Ar beam (10-12μm beam size) over the region of interest at relatively low angles (0-15°) [40]. The milling process can be conducted using moderate ion milling rates (1.66nm/min for Si at 900V and 15°) and also at relatively moderate ion beam current densities (~2pA/μm²). The main purpose of using a low energy focused Ar beam is to remove any kind of surface artifact (amorphous damage) in a reasonable time period without sacrificing any electron transparent area of the TEM sample.
Figure 2.10 Amorphous damage depth in single crystal Si as a function of Ga ion energy [36].

Figure 2.11 Amorphous damage depth in single crystal Si as a function of Ar ion energy and incidence angle [38].
In order to achieve this, a focused Ar ion beam as shown in Figure 2.12 (a) at proper milling voltage, milling angle and milling rate is applied to the TEM foil. A focused Ar beam avoids the problems that arise due to the geometry of the specimen, so that the Ar ion beam can easily reach to the surface of the specimen. This approach prevents the possible cross contamination caused from the surrounding factors such as the support Cu grid. During the milling process, the focused Ar ion beam is used for ion milling and at the same time for imaging and selection of the region of interest. The captured image is a scanning ion image, where the secondary electrons are collected to form the image. Figure 2.12 is the schematic of the system and a 500V Ar ion image showing the sample layout and the milling geometry. Milling process is achieved similar to the FIB box milling where the 10-12μm size focused ion beam is scanned over a selected box area.
Figure 2.12 (a) Ion milling geometry in the low energy Ar ion milling system (Nanomill\textsuperscript{TM} [40]) (b) 500V Ar ion image of the FIB lamella.
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[40] P. Fischione Fischione instruments Model 1040 NanoMill™

CHAPTER 3

LOW ENERGY ION MILLING

AND

FIRST RESULTS FROM AN ABERRATION CORRECTED STEM

3.1. Abstract

In the first part of this chapter, applications of a low energy Ar ion milling technique for Transmission Electron Microscope (TEM) sample preparation of various metallic alloys have been evaluated. The low energy/low angle milling process allows the amorphous material on the surface to be removed, so thin samples with damage free surfaces can be prepared. For this purpose a focused Ar ion beam system was applied to minimize the ion-induced artifacts generated due to the Focus Ion Beam (FIB) milling or Conventional Ion Milling (CIM) processes. The post milling structure of the TEM samples were examined at 300kV accelerating voltage using both an uncorrected FEI TITAN™ 80-300 S/TEM and a probe corrected FEI TITAN™ 80-300 S/TEM microscopes.

In the second part, initial results from a 300kV probe aberration corrected STEM microscope are presented demonstrating the important characteristics of the system and its capability in imaging and microanalysis of materials at high resolution.
3.2. TEM sample preparation using low energy Ar milling

3.2.1. Materials and milling parameters

In order to monitor the progress of the low energy milling treatments of TEM samples, we selected a wide range of materials that were either conventionally or FIB end milled. The materials and their milling parameters are briefly summarized in Table 3.1. The Renè 88DT sample is a Ni-based superalloy with major alloying elements Al, Cr, Co, Mo and W. It is used as a disk component in the turbine section of jet engines. Ti64 is mainly Ti containing 6wt%Al and 4wt%V and is another widely used alloy due to its high specific strength and favorable balance of properties for many varied applications. Ti5553 is a beta-stabilized titanium alloy with a composition of 5wt%Al, 5wt%V, 5wt% Mo and 3wt% Cr which in this work has been processed using LENS (Laser engineered net-shape processing). Finally, we have demonstrated the possible outcomes of the low energy ion milling process in preparation of sputter deposited metallic Ti/Nb multilayer sample in cross section.

The conventional samples were prepared by cutting 3mm disks, grinding to less than 80μm thickness, dimpling the center of the foils down to 20-25μm and 5 kV Ar ion milling to electron transparency. In contrast, the surfaces of FIB cut samples were first coated with a Pt protective layer and then Ga trenched milled at 30kV. For final milling stage, FIB-ed lamellae were welded to Cu grids and thinned at 30kV. In some cases, the surfaces of the prepared membranes were polished using a 5kV Ga ion beam. All the samples were further milled from both sides of the foils using low energy Ar milling.
<table>
<thead>
<tr>
<th>Sample</th>
<th>CIM*</th>
<th>FIB**</th>
<th>Low energy Ar milling</th>
<th>Imaging</th>
<th>Sample configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Renè88DT(1)</td>
<td>-</td>
<td>30kV</td>
<td>2kV</td>
<td>EFTEM</td>
<td>FIB lamella</td>
</tr>
<tr>
<td>Renè88DT(2)</td>
<td>5kV</td>
<td>-</td>
<td>900V/500V</td>
<td>HRTEM</td>
<td>3mm disc</td>
</tr>
<tr>
<td>Ti64</td>
<td>-</td>
<td>30kV</td>
<td>2kV/500V</td>
<td>HRTEM</td>
<td>FIB lamella</td>
</tr>
<tr>
<td>Ti/Nb</td>
<td>-</td>
<td>30kV/5kV</td>
<td>900V/500V</td>
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<tr>
<td>Ti5553</td>
<td>-</td>
<td>30kV</td>
<td>2kV</td>
<td>TEM</td>
<td>FIB lamella</td>
</tr>
</tbody>
</table>

*Conventional Ion milling (CIM)
**Focused Ion Beam (FIB)

Table 3.1 Materials and ion milling parameters.
ion milling energies have been determined at constant milling angle and milling box size. For this purpose, 20μm x 20μm box area on a Si <100> wafer surface was milled at 15° ion beam angle (with respect to the surface plane) and depth profiled using an Atomic Force Microscope (AFM). Figure 3.1 (a) shows 3D AFM surface topography of the milled area at 900V and 15° for 15hrs. Due to the 15° inclination of the ion beam, 20μm x 20μm box area was projected as 20μm x 80μm in size on the sample surface. The corresponding milling rates were measured by depth sectioning of the 3D AFM profiles for a given box area, voltage, beam current, incidence angle and time period. For example, at 900V, for a 20μm x 20μm milling box area, 200pA Ar ion current and 15° ion beam incidence angle the milling rate was measured as ~1.66nm/min for Si. The variation in the milling rate was plotted as a function of ion beam energy in Figure 3.1 (b). This plot evidently revealed the reduction in the milling rate by decreasing the ion beam energy. In the present work, the majority of the low energy Ar ion milling experiments was conducted at milling angles of +15°/-10°.

3.2.2. Low energy Ar ion milling results

The characteristics of the ion mill damage were first examined on Ni-based superalloy Renè 88DT sample. Figure 3.2 shows series of electron micrographs taken from the Ni-based superalloy at the different stages of the low energy ion milling treatment. The sample was first perforated for electron transparency at 5kV using a broad Ar ion beam. This milling step led to a surface damage layer as shown in Figure 3.2 (a), which was reduced in extent by low energy Ar milling. The low energy and low angle ion milling process was performed on the both sides of the TEM foil at an initial energy of
Figure 3.1 (a) 3D AFM depth profile of a 20x20μm milling box area at milling energy of 900V and incidence angle of 15° for 15 hrs (b) Measured milling rates (nm/min) for a 20x20μm milling box area and 15° beam incidence angle at various ion energies.
Figure 3.2 HRTEM images and corresponding Fast Fourier Transforms (FFTs) of conventional 3mm disc Ni-based superalloy Renè 88DT TEM sample after (a) 5kV Ar ion milling, (b) 900V Ar ion milling 20 minutes each side, (c) 500V Ar ion milling 20 minutes each side and (d) 2nm sized particle in the Ni matrix clearly visible after the final 500V milling cycle.
900V (Figure 3.2 (b)) and then 500V (Figure 3.2 (c)) at incident ion beam angles of +15/-10°. This process was carried out for 20 minutes on each side of the TEM foil at 900V and 500V milling energies. As seen from the HRTEM images, the gradual reduction of the ion acceleration voltage from 5kV to 900V and from 900V to 500V successfully diminished the surface mottling caused by the amorphous damage and consequently the lattice image clarity was markedly improved. This progress is also supported by the Fast Fourier Transforms (FFT’s) taken from the respective HRTEM images. The intensity of the spatial frequencies were enhanced by the gradual removal of the damage layer and there is a considerable decrease in the diffuse background of the FFT’s as well due to the reduction of the amorphous scattering from the surface damage layer. The low energy cleaning process also enabled the observation of nanoscale features such as a 2nm size particle nucleated in the matrix of the Ni-based superalloy as shown in Figure 3.2 (d).

Besides the HRTEM imaging, the 500V low energy milled Ni-based superalloy Renè 88DT sample was imaged using a probe aberration corrected STEM in the high angle annular dark field (HAADF) mode. Considering the contrast transfer function of HRTEM and STEM, HAADF STEM strongly represents the low spatial frequency information and therefore it is quite sensitive to the effects of the surface amorphisation. Figure 3.3 shows the probe corrected HAADF STEM image of ordered \( \gamma' \) (Ni$_3$Al) phase in the superalloy Renè 88DT sample and corresponding intensity profile integrated across the Ni and Al atomic columns. In Figure 3.3 (a), the Ni (Z=28) atomic columns appears bright and Al (Z=13) columns dark due to their atomic number difference: both of these types of columns of atoms contain appropriate solute atoms governed by sublattice
Figure 3.3 (a) Aberration – corrected HAADF STEM image of $\gamma'$ (Ni$_3$Al) precipitate in the superalloy Renè 88DT showing the ordering of the Ni (bright atomic columns) and Al (darker atomic columns) on the [100] zone axis after 500V Ar ion milling, (b) Intensity profile across the atomic columns of Ni and Al showing the amplitude change.
occupancy in this alloy. The profile clearly illustrates the intensity change through the atomic columns due to their atomic number difference. These results were consistent with the ordered nature of the $\gamma'$ (Ni$_3$Al) intermetallic structure.

The high-energy ion damage is often pronounced for 30kV FIB milled surfaces and so the influence of low energy milling on the 30kV FIB cut René 88DT and Ti64 alloy samples has been evaluated. These samples were 30x15$\mu$m FIB cut TEM lamellae, which were welded to Cu grids. Figure 3.4 shows the Energy filtered TEM (EFTEM) Cr elemental maps of the FIB cut René 88DT sample before and after low energy ion milling applications. The Cr elemental distribution and $\gamma'$ precipitate size and density in this alloy is critical for material performance under high-temperature environments and consequently fine $\gamma'$ precipitates (dark regions in Figure 3.4) that are relatively lean in Cr compared with the $\gamma$ matrix (light region) were imaged using Cr- L$_{23}$ ionization edge at an energy loss of 575eV. As seen in Figure 3.4 (b) the removal of the surface amorphous layer by low energy milling at 2kV significantly enhanced the resolution of the fine $\gamma'$ precipitates and yielded a more precise chemical and morphological representation of the microstructure.

In Ti64 sample, the change at edge of the FIB’d foil during the ion milling process was examined and the edge characteristic compared with the far edge imaging of the sample. Figure 3.5 shows the progress in HRTEM images of the foil edge after successive milling stages at different ion energies. As shown in Figure 3.5 (a) the initial 30kV Ga milling created a surface damage layer of about 30nm in thickness. Following 2kV low energy Ar milling reduced this damage layer down to thickness of ~5nm (Figure 3.5(b)). It is clear that low energy Ar ion milling process at 2kV has successfully
Figure 3.4 EFTEM Cr (L_{23} at 575eV) elemental map of Ni-based superalloy René 88DT after (a) 30kV FIB and (b) 2kV Ar ion milling.
Figure 3.5 HRTEM images showing the edge of the FIB foil after (a) 30kV FIB Ga ion milling, (b) 2kV Ar ion milling, and (c) 500V Ar ion milling.
removed the amorphous damage layer generated by the 30kV Ga milling process and the surface characteristic has become a combination of amorphous and crystalline transition region. Further milling of the sample at 500V removed this amorphous/crystalline transition region and damage free sample where the crystalline regions extended to the edge of the sample was obtained, as seen in Figure 3.5 (c). The characteristic of the damage layer in α-Ti has required a low energy-milling step at 500V so that the crystalline parts of the sample can be studied without any visible amorphous artifacts. These results were also confirmed by the HRTEM images taken from the far edge of the foil at different ion milling energies. Figure 3.6. (a), (b) and (c) reveals the improvement in HRTEM imaging of the α-Ti lattice structure of this alloy during the milling stages at 30kV FIB Ga ion milling, 2kV and 500V Ar ion milling. The surface mottling seen in Figure 3.6 (a) due to the 30kV FIB damage was reduced by Ar ion milling at 2kV, and final 500V milling removed the most of the amorphous damage resulting in a definite representation of the lattice structure.

As discussed above, the imaging by probe illumination may be more sensitive to the surface artifacts than the imaging by parallel illumination and this makes the STEM samples more demanding in terms of the surface quality. Figure 3.7 shows probe aberration corrected HAADF STEM images of a Ti/Nb multilayer sample before and after low energy Ar ion milling process and respective spatially resolved intensity profiles across the interface between Nb and Ti layers. As seen in Figure 3.7 (a) the STEM image indicates a very weak atomic column contrast from the both Nb and Ti layers due to the surface damage caused by the 5kV FIB milling. In addition to this, the background generated by the brighter (heavier) Nb atomic columns tends to swamp the
Figure 3.6 HRTEM images of the $\alpha$-Ti lattice structure in Ti64 alloy after, (a) 30kV FIB Ga ion milling, (b) 2kV Ar ion milling and (c) 500V Ar ion milling.
Figure 3.7 Aberration corrected HAADF STEM images and corresponding FFT’s of Ti/Nb multilayer interface after (a) 5kV FIB Ga ion milling, (b) After 900V/500V low energy Ar ion milling step and (c) Spatially resolved intensity profiles across the atomic columns of Nb and Ti after the respective milling processes.
darker (lighter) Ti atomic columns making the interface analysis difficult. Figure 3.7 (b) is the HAADF STEM image of the same foil after 900V /500V Ar ion milling steps. As seen in this image, the lattice structure of the both Nb and Ti layers and the interface between them are clearly resolved after the low energy milling of the sample. The spatially resolved intensity profiles across the atomic columns in Figure 3.7 (c) indicated reduced background and enhanced atomic column intensity for both Nb and Ti layers as a result of the low energy ion milling step. This reduction in the background intensity (due to the reduction in the amorphous damage) also enabled the imaging of the atomic columns of each layer in conjunction with the details of the interface structure.

Another Ga surface damage characteristic is the anomalous contrast known as “black dot” damage often observed in low magnification TEM imaging of the 30kV FIB milled samples. Figure 3.8 (a) shows the black dot damage in Ti5553 alloy after 30kV Ga milling process. This damage is thought to be due to the formation of secondary defects from the knock-on events and was successfully removed by 2kV low energy Ar ion milling of the sample as seen in Figure 3.8(b).

### 3.3. Aberration corrected STEM imaging

The basic principles of spherical aberration correction in the probe-forming lens of an electron microscope were briefly reviewed in Chapter 2. The correction of the third order spherical aberration allows a larger illumination aperture (larger convergence angle) to be used resulting in both improved resolution and increased electron beam current. The projected performance benefits from an aberration corrected probe are expected to be two fold: for imaging and for microanalysis.
Figure 3.8 Bright field TEM images of Ti5553 alloy showing (a) The 30kV FIB “black dot” damage (b) After 2kV low energy ion milling where the damage was removed and dislocation structure clearly revealed (small image).
The overall improvements in the aberrations of the probe-forming lens can be identified by characterizing the so called “Ronchigram” image, which is the shadow image of the probe on the sample [1]. Any significant aberration depending on its symmetry can be detected on this Ronchigram image. Figure 3.9 (a) is the Ronchigram image of the corrected electron probe focused on a thin amorphous C film showing the contrast free flat phase field extended up to ~60mrad half-angle. In the angular limits of the condenser apertures used for STEM imaging in the microscope (18mrad and 25mrad) this flat phase field did not reveal any effective aberrations. This simply indicates that the microscope STEM resolution is no longer limited with the aberrations of the probe-forming lens. The optimum convergence angle for an uncorrected TITAN S/TEM at 300kV and Cs of 1.2mm is 9mrad.

Figure 3.9 (b) is the simulated microscope transfer function (MTF) of the corrected probe at 2μm Cs, 2nm defocus and 18mrad beam convergence angle typically used on the corrector. The MTF clearly indicates that the sub-angstrom resolution can be achieved by minimizing the spherical aberration and defocus of the microscope. Practical consequence of aberration corrected STEM microscopy was tested on crystalline materials imaging down to their low order zone axis.

3.3.1. **First results from an aberration corrected STEM**

Due to its well-known crystal structure, single crystal Si is a common test material used in HAADF STEM and HRTEM resolution experiments. Si has a diamond crystal structure with a lattice parameter of 0.544nm and when oriented to a <110> zone axis it provides a characteristic atomic column configuration (dumbbells) where the atomic
Figure 3.9 (a) Ronchigram of the aberration corrected probe showing the flat phase field extended up to ~60mrad half-angle (b) Microscope transfer function (MTF) after aberration correction of the probe at 2μm C_s, 2nm defocus and 18mrad probe convergence angle.
Figure 3.10 (a) Probe aberration corrected HAADF STEM image of <110> Si dumbbells (b) FFT of this STEM image showing the sub-Angstrom spatial frequency.
spacing is 0.136nm. Figure 3.10(a) is a probe corrected HAADF STEM image of Si in the <110> orientation acquired using a 25mrad probe convergence angle. As seen in this image, the Si dumbbells were clearly resolved and there exists additional higher spatial frequency reflections on the FFT (Figure 3.10 (b)) from (551) and (440) planes at lattice spacing of 0.104nm and 0.96nm, respectively. Besides this improved resolution, the minimum distortion on the overall Si atomic column positions is a good indication of the improved stability of the stage. The additional streaks in the spatial frequencies perpendicular to the scan direction are thought to be either due to the scan noise generated in the system or due to the reduced Fourier convolution in the imaging process.

As mentioned above, correction of spherical aberration allows a larger aperture to be used in the probe-forming lens, resulting in improved resolution and beam current. Figure 3.11 (a) and (b) are the FFTs taken using 18mrad and 25mrad condenser apertures respectively. The FFT in Figure 3.11 (a) clearly shows that 18mrad aperture is diffraction limited providing less information transfer from the higher frequency reflections. In contrast, increasing the optimum aperture angle to 25mrad has brought additional high frequency information to the FFT in Figure 3.11 (b). The STEM image is a convolution of the probe intensity with the object information; therefore the shape of the probe is another important factor that influences image contrast. Figure 3.12 is a HAADF STEM image of the crystalline Si/ amorphous SiO₂ interface taken using 18mrad and 25mrad probe convergence angles where the probe aberrations are corrected up to 18mrad convergence angle. As compared with the 18mrad probe where the interface is sharp, imaging with a 25mrad aperture displays a broad interface extended over an area of few atomic columns. This difference in the image contrast shows the possibility of image
Figure 3.11 FFT's of the aberration corrected <110> Si HAADF STEM images recorded using (a) 18mrad probe convergence angle and (b) 25mrad probe convergence angle.
Figure 3.12 Aberration corrected HAADF STEM images of crystalline Si / amorphous SiO$_2$ interface acquired using (a) 18mrad probe convergence angle and (b) 25mrad probe convergence angle.
delocalization at the interface due to the intensity in the tails of the 25mrad probe [6]. The probe tail intensity alters the cross talk between the atomic columns and distributes the scattered column intensity over a finite distance. The high angle elastic scattering in STEM exhibits strong atomic number contrast, which is mainly scattering from the atomic nucleus through some screening from the core shell electrons. In this sense, Ni based superalloy Renè88DT has a very unique atomic structure for studying the high angle scattering contrast in uncorrected and aberration corrected STEM modes. Renè88DT microstructure consists of $\gamma'$-Ni$_3$Al ordered intermetallic precipitates dispersed in a $\gamma$-Ni solid solution matrix. Figure 3.13 shows the uncorrected and corrected images of the $\gamma'$-Ni$_3$Al/$\gamma$-Ni interface at 51-335mrad HAADF collection angle range for uncorrected and 46-325mrad range for corrected STEM modes. In the [110] zone axis projection of the ordered $\gamma'$-Ni$_3$Al unit cell, the Ni and Al (200) atomic planes alternate as bright, Ni and dark, Al atomic columns due to their atomic number difference. Figure 3.13(a) is an uncorrected image of the interface between $\gamma'$-Ni$_3$Al and $\gamma$-Ni collected using 9mrad convergence angle and beam current of 12pA. In contrast, the aberration corrected image in Figure 3.13 (b) was collected using 18mrad condenser aperture and beam current of 40pA. The comparison of these two images clearly indicated that the definition of the both interface and the atomic columns were improved by correcting the probe aberrations. This enhanced image contrast was also confirmed by the intensity profiles taken across the Ni and Al columns of uncorrected and corrected images as shown in Figure 3.14. The beam current was improved by a factor of ~4 using a larger condenser aperture and as a result the amplitude of the both Ni and Al atomic columns with respect to the background were enhanced in the corrected intensity profile.
Figure 3.13 HAADF STEM images of $<110>$ $\gamma'$-Ni$_3$Al/$\gamma$-Ni interface showing the image contrast obtained using (a) An uncorrected probe at 9mrad convergence angle and (b) A corrected probe at 18mrad convergence angle.
Figure 3.14 The HAADF STEM intensity profiles across the atomic columns of Ni and Al at the <110> orientation of γ'-Ni₃Al intermetallic compound acquired using (a) An uncorrected probe at 9mrad convergence angle and (b) A corrected probe at 18mrad convergence angle.
3.4. Discussions on low energy ion milling and aberration corrected STEM imaging

In the first part of Chapter 3, the successful application of a low energy Ar ion milling process in preparation of both FIB and conventional ion milled TEM samples has been demonstrated. This new technique is capable of removing most of the amorphous damage surface layer caused by high-energy ion milling processes (>5kV).

The low energy ion milling was tested on FIB Ga ion milled (30kV-5kV) or conventionally Ar ion milled (>5kV) TEM foils. The thickness of the amorphous damage layer for FIB’ed α-Ti (Ti64 alloy) sample at 30kV was measured as 30nm. By using low energy Ar ion milling this damage layer thickness was initially reduced down to 5nm at 2kV and finally at 500V a damage free sample was obtained. The gradual reduction in ion milling energy is intended to remove the amorphous damage layer created by the preceding milling process. The Ar ion milling energy for 30kV FIB finished surfaces was set as 2kV on the samples that were EFTEM and TEM imaged and an additional 500V final polishing applied on the samples HRTEM imaged. The milling steps for 5kV Ar and Ga milled surfaces were set as initial 900V milling followed by a polishing at 500V for the samples that were either high resolution STEM or TEM imaged. 500V milling was carried out as the lowest Ar ion energy for the removal of the amorphous surface damage layer. Similar low energy Ar ion milling experiments were also conducted in the literature at the energy range of 3kV to 120V. For example, Barna et al reported an amorphous layer thickness of 5nm at 3kV and 1nm at 250V for Si and 2.1nm at 3kV for GaAs [2]. Barna et al also did not observe any amorphous layer for GaAs at 250V and for Si at 120V Ar ion milling energies.
The thickness of the Ar induced amorphous damage that has been measured in α-Ti at 2kV was approximately 5nm, which is similar to the value of 5nm reported by Barna et al for Si at 3kV. However, their starting Ar ion energy for Si was 3kV where in our case we have started with an amorphous damage layer of around 20-30nm generated by the 30kV Ga ion beam. The typical 30kV FIB Ga ion damage reported for single crystal Si in the literature is approximately 30nm [9].

After the systematic reduction of the Ar ion energy down to 500V, the edge of the α-Ti in Ti64 foil showed no signs of amorphisation, which was further confirmed by the HRTEM imaging of the far edge of the sample. The thickness of the amorphous damage layer may vary from sample to sample depending on the composition and structure. However, the preliminary results in this work showed that a remarkable reduction in the surface amorphisation of the TEM foils can been achieved by using low energy ion milling process regardless of the composition and structure of the samples milled. In addition to these experimental observations, an attempt has been made to estimate the thickness of the amorphous damage layer using an empirical equation proposed by Barna et al [10].

\[ d = 20E^{0.6} \sin \theta \]  

(3.1)

This equation predicts the amorphous layer thickness \( d \) (nm) as a function of ion energy \( E \), (kV) and the incident ion beam angle \( \theta \), (degrees). Table 3.2 shows the comparison between the experimentally measured amorphous layer thickness using HRTEM imaging and the values of the predicted amorphous layer thickness calculated using equation (3.1) for α-Ti in Ti64 alloy FIB sample at accelerating voltages of 30kV, 2kV and 500V and incident ion beam angle of 10°. As seen in Table 3.2 the predicted
<table>
<thead>
<tr>
<th>Ion energy (kV)</th>
<th>Experimental</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
<td>0.5</td>
<td>$\leq 2$</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 3.2 Amorphous damage depth vs. ion beam energy in $\alpha$-Ti.
values of amorphous damage depth (thickness) agree well with the experimental results further confirming the successful reduction of the damage layer at reduced ion energies.

As previously mentioned, we would expect STEM imaging to be more sensitive to any surface amorphisation than HRTEM. Figure 3.15 is the comparison of the microscope contrast transfer function of HRTEM and STEM. As seen in this plot, HRTEM acts as a band pass filter by removing the low frequency information, which may lead to an artificial sharpening of the image. So far, low energy Ar ion milling (<900V) of the conventionally ion milled samples (5kV) and FIB milled samples (30kV and 5kV) revealed a significant improvement both in the atomic resolution STEM and HRTEM imaging of the samples. The removal of the amorphous layer also reduces the total sample thickness and might help the imaging process by reducing the background intensity. Besides the ion milling energy, ion beam incidence angle is considered to be an important parameter can affect the sample quality. From these first results no change in the quality of the TEM foils at the ion beam angle range of 10-15° was observed.

In the second part, initial results from a probe aberration corrected 300kV FEI TITAN S/TEM were presented and compared with the results obtained from an uncorrected 300kV FEI TITAN S/TEM system. These preliminary results indicated that when the spherical aberration of the probe-forming lens was corrected, both the image contrast and the resolution of the microscope were improved [4]. This enhanced performance suggests that wider range of atomic number elements in relatively thicker TEM foils can be imaged at an improved resolution using the probe aberration corrected HAADF STEM mode. Aberration correction changes the experimental parameters by modifying the probe characteristics, such as the intensity, width and shape of the probe;
Figure 3.15 Microscope contrast transfer function of STEM and HRTEM [7].
therefore these modifications on the probe characteristic should be considered when interpreting the image contrast and microanalytical data.

The resolution and image contrast that can be obtained at different probe parameters was evaluated by imaging a <110> oriented Si single crystal in the STEM mode. In case where a large probe convergence angle was used the image resolution was improved significantly. At 25mrad probe convergence angle, Si (440) spatial frequency and d spacing of 0.96nm was observed indicating a sub-Ångstrom probe size. Another benefit of using a larger convergence angle was improved beam current, which means increased signal for both imaging and analytical applications. For instance, at probe size of 0.12nm about 4 times more current has been measured for a corrected probe at 18mrad convergence angle than an uncorrected probe at 9mrad convergence angle. A possible drawback of using a larger convergence angle was observed while imaging the crystalline Si/ amorphous SiO₂ interface. The interface appeared sharp at the probe convergence angle of 18mrad (where the probe aberrations are corrected up to 18mrad) and broader at the probe convergence angle of 25mrad. This result shows the contribution of the probe tail intensity to the image contrast at 25mrad convergence angle by spreading the scattering intensity over the atomic columns [5,6]. Figure 3.16 is the simulated probe intensity profiles of the corrected probe at 2μm Cₙ 300kV accelerating voltage and varying convergence angle and defocus values. As seen in this Figure, FWHM of the probe intensity is evidently reduced by using a larger convergence angle (25mrad) resulting a better resolution in the STEM imaging mode, but this kind of illumination condition has also significantly increased the probe intensity at the probe tails which might consequently delocalize the specimen information on the atomic columns.
Figure 3.16 Simulated probe spread functions (semi probe intensities) of the corrected probe at 2μm $C_s$, 2nm, 4nm defocus and 18mrad, 25mrad convergence angle values.
Besides the convergence angle, the increase in defocus has also altered the probe tail intensities and this effect is more pronounced at a larger convergence angle value (Figure 3.16). This result suggests that the optimum condition for aberration corrected STEM imaging becomes a compromise between minimizing intensity in the probe tails and achieving a small probe width [8].

References

CHAPTER 4

CHARACTERIZATION OF PHASE STABILITY IN NANOSCALE METALLIC MULTILAYERS

4.1. Abstract

When thin films are deposited on suitable substrate surfaces, they often exhibit crystal structures that would be metastable for the same materials in the bulk form [1]. As described in Chapter 1, these metastable structures exist in the nanometer or sub-nanometer regime and the factors underlying these transitions are regarded as being thermodynamic in nature. The new characterization tools allow direct imaging and analysis of such materials and link the performance variations with the crystal structure and composition variations.

In this chapter, the structural and compositional variations will be addressed as a function of length scale in nanoscale Cu/Nb and Ti/Nb metallic multilayers. Crystal and interface structure of the layers were characterized using electron beam and X-ray based techniques whereas the chemical composition of the multilayers at varying thickness were probed using complimentary techniques of XEDS, EELS and 3D atom probe microanalysis.
4.2. Cu/Nb multilayers

The room temperature equilibrium crystal structure of Cu is face centered cubic (fcc) with a lattice parameter of 0.360nm and for Nb it is body centered cubic (bcc) with a lattice parameter of 0.330nm. fcc Cu and bcc Nb are mutually immiscible and neither Cu nor Nb exhibits an allotropic transformation to a higher temperature phase. However, Kung et al have reported stabilization of bcc Cu in sputtered deposited Cu/Nb metallic multilayers upon reducing the Cu layer thickness below a critical value [1]. In their work, the authors deposited a series of Cu/Nb multilayer films with layer thicknesses changing from 1.2nm to 100nm while keeping the volume fraction of the two phases constant at 50%. Upon reducing the bilayer thickness to ~2.4nm (1.2nmCu/1.2nmNb), the transformation of stable fcc Cu/ bcc Nb structure to pseudomorphic bcc Cu/bcc Nb structure was observed. The lattice parameter of bcc Cu was reported as being $3.28\pm0.05\text{Å}$.

Similar phase transformations in nanoscaled metallic multilayers have been examined as functions of bilayer thickness and volume fraction of the constituent layers, and often explained by reference to a classical thermodynamical model [2,3]. In this classical thermodynamic model, pseudomorphic phases are stabilized by the competition between the volumetric (positive) and interfacial (negative) components of the total free energy. It appears that at a critical transition thickness, the decrease in the interfacial free energy component more than compensates for the increase in the volumetric free energy component, and consequently a pseudomorphic phase can be stabilized.
4.3. bcc Cu in Cu/Nb multilayer system

Following the classical thermodynamical mode described by Dregia et al. [2], the total free energy change per unit area $\Delta g$ of a structural transition $\text{fcc Cu/bcc Nb}$ to $\text{bcc Cu/bcc Nb}$ can be given by:

$$\Delta g = \Delta G_{\text{Cu}} (1 - f_{\text{Nb}}) \lambda + 2 \Delta \gamma_{\text{bcc/bcc}}$$

(4.1)

Where $\Delta G_{\text{Cu}}$ is:

$$\Delta G_{\text{Cu}} = (G_{\text{fcc}}^{\text{Cu}} - G_{\text{fcc}}^{\text{Cu}})$$

(4.2)

And $\Delta \gamma_{\text{bcc/bcc}}$ is:

$$\Delta \gamma_{\text{bcc/bcc}} = (\gamma_{\text{bcc/bcc}} - \gamma_{\text{fcc/fcc}})$$

(4.3)

The occurrence of the allotropic phase transformation in Cu can be represented by the biphase diagram. Figure 4.1 is the established Nb rich part of the biphase diagram using the results of Kung et al. in combination with the series deposited multilayers in the present work. The volume fractions and bilayer thickness of each film were listed in Table 4.1. In this diagram (Fig.4.1) the slope of the biphase boundary can be written as:

$$m = \frac{\Delta G_{\text{Cu}}}{\Delta \gamma_{\text{bcc/bcc}}}$$

(4.4)

In this first approximation of the biphase diagram, the effect of coherency strain has been ignored and all contributions that scale with volume are contained in $\Delta G$ term and all contributions that scale with area are contained in $\Delta \gamma$ term. In order to construct the Nb rich part of the biphase diagram series of Cu/Nb metallic multilayers were deposited for which the bilayer thicknesses and Nb volume fractions were varied.
Figure 4.1 Biphase stability diagram of the Cu/Nb multilayer system as a function of volume fraction and bilayer thickness.
<table>
<thead>
<tr>
<th>Multilayer</th>
<th>$\lambda$</th>
<th>$f_{\text{Nb}}$</th>
<th>Crystal structure (Cu/Nb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>27</td>
<td>0.44</td>
<td>fcc/bcc</td>
</tr>
<tr>
<td>#2</td>
<td>19.2</td>
<td>0.62</td>
<td>fcc/bcc</td>
</tr>
<tr>
<td>#3</td>
<td>15.6</td>
<td>0.77</td>
<td>fcc/bcc</td>
</tr>
<tr>
<td>#4</td>
<td>13.8</td>
<td>0.87</td>
<td>fcc/bcc</td>
</tr>
<tr>
<td>#5</td>
<td>10</td>
<td>0.93</td>
<td>bcc/bcc</td>
</tr>
<tr>
<td>#6</td>
<td>9.5</td>
<td>0.96</td>
<td>bcc/bcc</td>
</tr>
<tr>
<td>#7</td>
<td>4.4</td>
<td>0.73</td>
<td>fcc+bcc/bcc</td>
</tr>
<tr>
<td>#8</td>
<td>4.5</td>
<td>0.78</td>
<td>bcc/bcc</td>
</tr>
<tr>
<td>#9</td>
<td>10.4</td>
<td>0.89</td>
<td>fcc/bcc</td>
</tr>
<tr>
<td>#10</td>
<td>5.3</td>
<td>0.66</td>
<td>fcc/bcc</td>
</tr>
<tr>
<td>#11</td>
<td>8.7</td>
<td>0.57</td>
<td>fcc/bcc</td>
</tr>
</tbody>
</table>

Table 4.1 List of the deposited Cu/Nb multilayers
The reported \(bcc\) Cu transition point at 50\% volume fraction by Kung et al was displayed as an open square on the biphase diagram [1] and based on this data point a biphase boundary for \(bcc\) Cu transformation can be predicted. As seen in Figure 4.1 the Nb rich part of the biphase boundary is linear in the absence of coherent strains and reveals the phase stability regions of \(fcc\) Cu and \(bcc\) Cu at varying volume fractions of Nb. Each data point in the phase stability region was confirmed using X-ray diffraction (XRD) and plan-view electron diffraction techniques. Figure 4.2 (a) and (b) are the reflection XRD pattern results from the data points represented as #10 and #8 in the biphase diagram. The XRD pattern in Figure 4.2 (a) indicates that at bilayer spacing of 5.3nm, the layers show stable \(fcc\) Cu and \(bcc\) Nb phase structure. The diffraction intensities of \(fcc\) \{111\} Cu and \(bcc\) \{110\} Nb on the XRD pattern represents the energetically favorable closed pack planes. The satellite peaks originated from the modulation in the layer structure are also marked on the diffraction pattern.

As the bilayer thickness was reduced to a value of 4.5nm, the \(fcc\) Cu/\(bcc\) Nb multilayer transformed to a \(bcc\) Cu/\(bcc\) Nb structure. This transformation occurred at a volume fraction, \(f_{Nb}\) of 0.78. Figure 4.2 (b) shows the single diffraction peak intensity corresponding to \{110\} closed pack planes of Nb and no \(fcc\) Cu planes were observed in this reflection XRD pattern. These XRD results were further confirmed by the plan-view electron diffraction observations. Figure 4.3 is the plan-view electron diffraction patterns from the data points of #10 and #8 on the Cu/Nb biphase diagram. The diffraction pattern of multilayer #10 in Figure 4.3 (a) was indexed as diffraction rings corresponding to the \(fcc\) Cu and \(bcc\) Nb crystal structures.
Figure 4.2 Reflection XRD patterns for Cu/Nb multilayer (a) #10, \{110\} \textit{bcc} Nb and \{111\} \textit{fcc} Cu peak intensities are shown (b) #8, single \{110\} diffraction peak intensity is indicated for both Cu and Nb.
Figure 4.3 Plan-view electron diffraction patterns for Cu/Nb multilayer (a) #10, indexed as fcc and bcc and (b) #8, indexed as coherent bcc/bcc structure.
At reduced bilayer thicknesses, the plan-view electron diffraction pattern was indexed as fully coherent \textit{bcc} crystal structure without any major diffraction rings from the \textit{fcc} Cu as shown in Figure 4.3 (b). The plan-view electron diffraction results supported the XRD results and also confirmed the formation of coherent \textit{bcc}/\textit{bcc} structure at reduced bilayer thickness. The calculated lattice parameter for \textit{bcc} Cu is similar to lattice parameter value of \textit{bcc} Nb, which is \( \sim 0.330 \text{nm} \).

The growth morphology of the layers and their crystal structure were investigated at the cross-section view in the TEM. HAADF STEM was the choice of technique in cross-section characterization of Cu/Nb multilayers due to its unique image properties as briefly described in the content of Chapter 2. Figure 4.4 shows the HAADF STEM images of the \textit{fcc} Cu/\textit{bcc} Nb multilayer #11 and \textit{bcc} Cu/\textit{bcc} Nb multilayer #8, respectively. The Nb (Z=41) layers appear bright due to their higher atomic number and Cu (Z=29) layers appear dark. The overall thin film morphology in these images reveals sharp interfaces between the layers. The individual layer thicknesses of the films were measured from the intensity profiles acquired from the HAADF STEM images, and peak-to-peak values of these intensities were used for bilayer thickness calculations and FWHM of the peaks for the individual layer thickness calculations. The detail of this layer measurement technique is addressed in the following sections where the layer thicknesses from complementary techniques have been compared.

Figure 4.5 (a) is the high resolution Z-contrast HAADF STEM image of the \textit{bcc} Cu/\textit{bcc} Nb multilayer #8. The image is background subtracted in order to improve the image clarity. Each dot in this high-resolution STEM image
Figure 4.4 Cross-section view HAADF STEM images of the Cu/Nb multilayer (a) #11 at bilayer spacing of 8.7nm and (b) #8 at bilayer spacing of 4.5nm.
Figure 4.5 Cross-section view HAADF STEM images of the Cu/Nb multilayer #8 (a) showing the ABAB bcc stacking of the \{110\} atomic planes in the Cu layer and (b) HAADF intensity profile across the atomic columns of \textit{bcc} Cu.
represents atomic columns of Nb and Cu, respectively and the intensity of each atomic column strongly depends on its atomic number owing to the high angle elastic (Rutherford) scattering process. Therefore the bright dots represent the atomic columns of Nb and relatively darker dots atomic columns of Cu. In this [111] zone axis orientation, Nb follows the ABAB stacking of the {110} atomic planes and across the Cu layer the same stacking sequence continues and reveals the ABAB bcc stacking of the Cu layer at the cross-section view as indicated in the image.

Figure 4.5 (b) is a line intensity profile integrated through the bcc Cu layer giving approximately 4 {110} atomic planes of bcc Cu at a total layer thickness of about 1nm. As mentioned in chapter 2, HAADF STEM is an incoherent imaging process providing direct interpretation of the images and it does not exhibit any delocalization effects, which also makes the interface structure imaging possible at atomic resolution. Figure 4.5 (a) clearly reveals a coherent interface between the bcc Cu and bcc Nb layers confirming the plan-view electron diffraction observations. From the both cross-section TEM and XRD results, the orientation relationship between bcc Cu and bcc Nb upon transformation was deduced as:

\[ \{110\}_{\text{bcc}} / \{110\}_{\text{bcc}} \]

\[ <111>_{\text{bcc}}/<111>_{\text{bcc}} \]

4.4. \textit{fcc Cu/bcc Nb multilayers}

The bulk stable form of \textit{fcc} Cu transforms to a \textit{bcc} Cu phase upon reducing the bilayer thickness and this transformation was confirmed using complementary characterization techniques. At reduced bilayer thickness the Cu/Nb layers form a
coherent bcc/bcc structure. The classical thermodynamic model explains this phase change through the competition between the volumetric and the interfacial energies of the stable and metastable phases, therefore it is critical to determine the bulk and interface properties of each form.

The XRD result in Figure 4.2 has already showed that the bulk equilibrium of fcc Cu and bcc Nb grew in a texture orientation with their lowest energy close packed planes \{110\} Nb and \{111\} Cu parallel to each other. Figure 4.6 is a cross-section HAADF STEM image of the fcc Cu/bcc Nb multilayer #11 and the corresponding FFT’s showing the layers of fcc Cu and bcc Nb at the bilayer spacing of 8.7nm. It is clear from this high-resolution STEM image that the close packed \{110\} Nb planes with ABAB stacking and \{111\} Cu planes with ABCABC stacking are parallel to each other and revealing the energetically favorable Kurdjumov–Sachs orientation:

\[ \{110\}_{\text{bcc}} / \{111\}_{\text{fcc}} \]
\[ <111>_{\text{bcc}} / <110>_{\text{fcc}} \]

The lattice mismatch between the fcc Cu and bcc Nb in this orientation is 11%.

The important details of the bulk and interface structure were also characterized in the STEM imaging mode. The lattice spacing of \{110\} planes in bcc Nb is 0.23nm. However, the detailed FFT analysis of the Nb layer in Figure 4.6 (b) indicated a d spacing of \( \approx 0.208 \text{nm} \) for the set of \{110\} planes that were tilted 30° with respect to the Cu/Nb interface. This deviation from the bulk \{110\} d spacing of bcc Nb may be due to the strain imposed from the template fcc Cu layer onto the bcc Nb layer. The calculated strain in this direction from the FFT analysis of the Nb layers is approximately 9.5%.
Figure 4.6 (a) Cross-section view HAADF STEM images of the Cu/Nb multilayer #11 and corresponding FFTs taken from (b) bcc Nb layer, (c) fcc Cu layer close to the interface and (d) fcc Cu away from interface.
The predicted strain in this direction is approximately 9.5%, which is projected on the planes from 11% in plane strain between the fcc Cu and bcc Nb based on the Kurdjomov–Sachs orientation.

As noted the lattice mismatch between fcc Cu and bcc Nb exhibited an in-plane strain which was taken up by the Nb layers. Surprisingly, Cu {200} planes were parallel to the strained Nb {110} planes as displayed in Figure 4.6 (a). Cu d spacing between {200} planes is ~0.18nm. The misfit between the atomic planes of {200} Cu and the strained {110} Nb is ≈13% which implies that every ~6 atomic planes there should be a misfit dislocation at the interface. The detailed HAADF STEM imaging of the interface between fcc Cu and bcc Nb is given in Figure 4.7. The image shows a smooth interface decorated by misfit dislocations separated about 6 {200} atomic planes of fcc Cu. The observed registry of Nb and Cu atomic columns in combination with the misfit dislocations at the interface suggested that the interface between the fcc Cu and bcc Nb is semi-coherent.

4.5. bcc Ti in Ti/Nb multilayer system

Recently, Thompson et al have reported the formation of bcc Ti in the Nb rich side of the Ti/Nb multilayer system [4]. Upon reduction in the bilayer thickness, bulk stable hcp Ti/bcc Nb transforms to a coherent bcc Ti/bcc Nb phase. Also, in their 3D atom probe analysis, these authors observed ~15 at% Nb mixing into the Ti layers in the bcc Ti/bcc Nb multilayer. In this present work, we have prepared several TEM samples in the cross section view and characterized the layer and interface structures of the Ti/Nb
Figure 4.7 Cross-section view HAADF STEM images of the Cu/Nb multilayer #11 showing the misfit dislocations at the interface of fcc Cu and bcc Nb.
multilayers either in their bulk or pseudomorphic forms. HAADF STEM was the choice of technique in imaging the cross-section TEM foils prepared from the hcp Ti/bcc Nb and bcc Ti/bcc Nb phase regions of the Ti/Nb biphase diagram.

First of all, there appears to be a difference in the determination of layer thicknesses between the work of Thompson et al and the present study, where such thicknesses have been determined using STEM intensity profiling. Thompson et al used XRD for bilayer thickness determinations and SEM EDS for individual layer thickness measurements and the details of these measurements have been discussed elsewhere [5]. In the present work, for each multilayer sample, an HAADF STEM image was acquired where the contrast is strongly atomic number dependent and then the intensity changes perpendicular to the layer interfaces were integrated over a certain area as shown in Figure 4.8 (a). Figure 4.8 (b) is the spatially resolved intensity profile plotted across the layers of bcc Ti and bcc Nb in Ti/Nb multilayer. In this profile, intensity oscillations at a frequency of 0.23nm indicate the scattering from the atomic columns whereas the change in the amplitude (e.g. I_{Nb}) of these oscillations reveals the atomic number difference between the atomic columns of Nb and Ti. The relative HAADF image intensity is proportional to the square of the atomic number Z and therefore Nb (Z=41) scatters 3 times more than Ti (Z=22), and 2 times more than Cu (Z=29). Since the heavier elements scatter more than the lighter elements, the associated background intensity (I_B) due to the sample thickness develops more effectively for Nb than the Ti. The thickness of the layers can be determined by either measuring the Full Width Half Maximum (FWHM) of these background intensities or by counting the amplitude of the corresponding elements in the HAADF intensity profile.
Figure 4.8 (a) STEM HAADF image showing the intensity integrated area (b) HAADF intensity profile across the atomic columns of \textit{bcc} Ti and \textit{bcc} Nb in Ti/Nb multilayer #8 indicating the bilayer and layer thickness.
By using the layer thickness values obtained from the STEM image intensity profiles, we have modified the Nb rich part of the Ti/Nb biphase diagram as shown in Figure 4.9. The new slope of the biphase diagram was increased with respect to the biphase boundary that was previously reported by Thompson et al. The calculated bilayer thickness values in the present work were located with a star mark next to them on this biphase diagram. Figure 4.10 is the HAADF STEM image of the Ti/ Nb multilayer #6 showing the coherent bcc Ti/bcc Nb lattice structure at a bilayer thickness of 5.3nm. The layer thickness of this multilayer was measured as 2nm bcc Ti and 3.3nm bcc Nb from the FWHM of the HAADF intensity profile. The orientation relationship in this coherent bcc/bcc structure was deduced as:

\[
\{110\}_{bcc} / \{110\}_{bcc} \\
<111>_{bcc} / <111>_{bcc}
\]

In Figure 4.10, the darker dots represents the Ti atomic columns indicating the characteristic bcc ABAB atomic stacking through the closed packed \{110\} planes whereas the brighter dots are the Nb atomic columns revealing the bcc ABAB stacking as well. The interface between the bcc Ti and bcc Nb is coherent. At a layer thickness of 2nm, hcp Ti transform to a bcc structure with Nb lattice parameter of 0.330nm resulting in negligible coherency strains. The layer thickness at which hcp Ti transformed to a pseudomorphic bcc Ti phase was measured as 2nm for the Ti/Nb multilayer #6 in the biphase diagram. This value is close to the reported value of 1.55nm bcc Zr in Zr/Nb multilayer system by Lowe and Gaballe [6], but different than the 3nm bcc Ti value reported by Thompson et al. Using the slope of this modified biphase boundary we have estimated the interfacial free energy change for the bcc/bcc transformation.
Figure 4.9 Biphase stability diagram of the Ti/Nb multilayer system as a function of volume fraction and bilayer thickness.
Figure 4.10 Cross-section view HAADF STEM image of the Ti/Nb multilayer #6 showing the coherent bcc Ti / bcc Nb structure.
In this case the slope of the biphase boundary is given by:

\[ m = \frac{\Delta G_{T_i}}{\Delta \gamma_{\text{bcc/bcc}}} \quad (4.5) \]

Based on the atom probe and EELS composition profile results, the equilibrium volumetric free energy difference between bcc Ti and hcp Ti has been calculated considering the \( \sim 15 \) at % Nb intermixing into the Ti layers. Using \( \Delta G_{\text{Ti-15Nb}} = 1.5 \times 10^8 \text{ J/m}^3 \) from CALPHAD calculations [5] and the slope of the biphase boundary reported in the present work, the interfacial free energy difference \( \Delta \gamma_{\text{bcc/bcc}} \) between the bcc Ti/bcc Nb and hcp Ti/bcc Nb was calculated as approximately \(-141 \text{mJ/m}^2\). The reported orientation relationship of hcp Ti/bcc Nb layers by Thompson et al is the Burgers orientation relationship:

\[ \{110\}_\text{bcc} / \{0001\}_\text{hcp} \]

\[ <111>_{\text{bcc}} / <1\overline{1}20>_{\text{hcp}} \]

In this orientation the lattice mismatch between the \{110\} bcc Nb and \{0001\} hcp Ti close packed planes is \( \sim 3\% \).

### 4.6. Composition stability in nanoscale metallic multilayers

The applicability of biphase diagrams has been successfully demonstrated in the Cu/Nb multilayer system. It appears that upon reduction in the bilayer thickness, fcc Cu/bcc Nb transforms to a coherent bcc Cu/bcc Nb phase. At large bilayer thickness, the interface structure between fcc Cu and bcc Nb was smooth and exhibited a semi-coherent interface decorated by an array of misfit dislocations. These preliminary results clearly
indicated that on reducing the bilayer thickness, the \textit{fcc} Cu to \textit{bcc} Cu structural transformation was accompanied by a higher energy \textit{semi-coherent fcc/bcc} interface to a lower energy \textit{coherent bcc/bcc} interface transformation.

Besides the bulk and interface structural stability in the metallic multilayers, the chemical or the composition stability is another important issue that should be considered when determining the thermodynamic variables $\Delta G$ and $\Delta \gamma$ terms. The composition stability can be defined as the amount of elemental mixing in the multilayers as a function of the length scale. Preliminary work by Thompson et al has already shown that there is a significant amount of intermixing (~15at% Nb into \textit{bcc} Ti), which is expected to influence both interfacial and bulk free energies [4,5]. The characterization of such changes in the composition of the layers will help to improve the accuracy and predictability of the biphase diagrams.

In the following, the composition changes in the metallic multilayers are addressed as a function of length scale and report on systematic probing of the elemental distribution in Cu/Nb and Ti/Nb multilayers. The techniques that employed have already been described in the content of Chapter 2. Basically, complementary techniques are employed, namely: STEM EDS/EELS and 3D Atom probe analysis. These techniques were applied for characterization of nanoscale metallic multilayers and the reliability of composition profiles was discussed considering the limits and capability of the each technique.
4.6.1. Calculation of k factors for XEDS analysis

In order to quantify the elements present in the specimen under the electron beam, it is necessary first to define a relationship between the composition of the elements and the detected intensities of the characteristic peaks of the employed spectroscopic technique. Cliff and Lorimer proposed a simple relationship for X-ray intensities of XEDS spectrum, which is known as the Cliff-Lorimer equation \[7\]. This approach relates the integrated intensities of the characteristic peaks of element A and B to the compositions of the elements by simply multiplying with a sensitivity term called the “Cliff-Lorimer factor” or k-factor. For a binary A-B system, this relation is given by:

\[
\frac{C_A}{C_B} = k_{AB} \left( \frac{I_A}{I_B} \right)
\]  

(4.6)

Where,

\[C_A + C_B = 1\]  

(4.7)

This proposed analysis ignores the correction of absorption and fluorescence for the samples, which are assumed to be sufficiently thin, and the correction is mainly done for atomic number. The Cliff-Lorimer factor can be determined either experimentally or theoretically and often experimental measurements are preferred over theoretical calculations since experimental conditions and detector parameters can vary for every microscope. For the given experimental conditions the samples under the electron beam were used to extract the k-factors for an A/B multilayer system. Assuming the sample thickness is constant over the area of interest, a relationship is defined between the total detected X-ray intensity in the analyzed volume and the composition. If the ratio of the
layer thickness is defined as $f_S$:

$$f_S = \left( \frac{h_A}{h_B} \right)$$  \hspace{2cm} (4.8)

Where $h_A$ and $h_B$ are the layer thickness of A and B in the multilayer stack respectively. The experimental k-factor can be written as,

$$k_{AB} = \left( \frac{I_{A_{\text{Total}}}}{I_{B_{\text{Total}}}} \right)$$  \hspace{2cm} (4.9)

Where $I_{A_{\text{Total}}}$ and $I_{B_{\text{Total}}}$ are the sum of the total integrated intensities of element A and B over equal total number of A and B layers in the multilayer stack. Using this approach and by knowing accurately the individual layer thicknesses, an estimate of the k-factors for atomic% composition calculations can be made. The calculated K line X-ray k-factors for the Cu/Nb and Ti/Nb are 0.40 and 0.64, respectively, as shown in Table 4.2. Theoretical k-factors were also calculated and listed in this table. The details of the theoretical calculation have been discussed elsewhere [7]. As seen in Table 4.2, there is a good agreement between the experimental and theoretical calculations of the k factors.

### 4.6.2. Calculation of $\sigma_A / \sigma_B$ factors for EELS analysis

As similar approach presented above can be applied for quantification of EELS intensities at a given collection semi-angle, $\beta$ (mrad) and energy window range, $\Delta$ (eV) and the composition ratio of elements A and B can be related to the edge intensity as [8]:

$$\frac{N_A}{N_B} = \frac{I_A(\beta\Delta)\sigma_B(\beta\Delta)}{I_B(\beta\Delta)\sigma_A(\beta\Delta)}$$  \hspace{2cm} (4.10)

Where,
<table>
<thead>
<tr>
<th>Multilayer</th>
<th>Experimental $k^K$ factor</th>
<th>Theoretical $k^K$ factor</th>
<th>Experimental $\sigma^L/\sigma^M$ factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Nb multilayer</td>
<td>0.40</td>
<td>0.37</td>
<td>0.04</td>
</tr>
<tr>
<td>Ti/Nb multilayer</td>
<td>0.64</td>
<td>0.59</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 4.2 Experimentally and theoretically calculated XEDS K line X-ray intensity k-factors and experimental EELS Cu and Ti L and Nb M edge partial ionization cross section ratios for Cu/Nb and Ti/Nb multilayers.
\[ N_A + N_B = 1 \]  \hspace{1cm} (4.11)

Here, \( N_A/N_B \) ratio can be considered to be essentially the same as the \( C_A/C_B \) ratio and the ratio of partial cross-sections \( \sigma_A / \sigma_B \) as Cliff-Lorimer factor, \( k \). The sensitivity factor for EELS can be accurately calculated from an experimental spectrum.

Figure 4.11 is the background subtracted EELS spectra acquired from the Ti/Nb and Cu/Nb multilayers representing the characteristic ionization edges of Nb M at 205eV, Cu L at 931eV and Ti L at 456eV energy losses. The values for the partial cross section of elements at these energy losses were calculated using the Hartree-Slater model fit on the ionization edges using the GATAN Digital micrograph software package. The details of this calculation have been reported elsewhere [9]. After appropriate background subtraction, the \( \sigma^L / \sigma^M \) ratios are estimated as 0.04 for Cu/Nb multilayers and 0.24 for Ti/Nb multilayers at 20mrad collection semi-semi angle and 40eV integrated energy window range as shown in Table 4.2.

### 4.6.3. Composition variations in Ti/Nb multilayer system

The stable form of the Ti is \( hcp \) and Nb is \( bcc \) and in a solid solution Nb acts as a \( bcc \) \( \beta \)-Ti stabilizer. In the multilayer form, when Ti layer thickness is reduced to 2nm, stable \( hcp \) Ti transforms to a metastable \( bcc \) Ti structure and Thompson et al have explained this transformation in metallic multilayers using a classical thermodynamic model [3]. Both X-ray and EELS line profiles were simultaneously acquired from the cross-sectional TEM sample of Ti/Nb multilayers, and using the measured k-factor for XEDS and \( \sigma_{Ti}^L / \sigma_{Nb}^M \) for EELS composition profiles were constructed.
Figure 4.11 Characteristic EELS ionization edges of (a) Nb M at 205eV (b) Cu L at 931eV and (c) Ti L at 456eV energy losses.
Figure 4.12 is the comparison of the XEDS and EELS profiles from a \textit{bcc} Ti /\textit{bcc} Nb multilayer #8 where the layer thickness are 1.8nm Ti and 2.1nm Nb, respectively. At this length scale, the XEDS profiles indicated equal amounts of Ti and Nb mixing into the neighboring layers and also significantly different composition variation than that suggested by the EELS profile. The EELS composition profile has revealed \(~15\) at\% Nb mixing into Ti and almost no Ti mixing into the Nb.

As mentioned before, Thompson et al had conducted atom probe composition profiles from similar layer thickness of \textit{bcc} Ti/\textit{bcc} Nb multilayer (2nm \textit{bcc} Ti and 3nm \textit{bcc} Nb) and indicated \(~15\)% at Nb mixing into the Ti layers and no Ti mixing into the Nb layers [4]. There is a good agreement between the EELS composition profiles of this work and the atom probe composition profiles reported by Thompson et al as shown in Figure 4.13. The agreement between the results of EELS and atom probe analysis suggests a possibility of \textit{beam broadening} for XEDS profiles at this layer thickness values.

At a relatively larger layer thickness  (7nm Ti/ 9nm Nb), both XEDS and EELS composition profiles revealed similar composition variations, as shown in Figure 4.14 and exhibited essentially no Nb mixing into Ti and also no Ti mixing into the Nb layers. It has been argued by Thompson, et al, that the intermixing of Nb into layers of \textit{bcc} Ti is due to the increased thermodynamic stability of this phase from the addition of \textit{bcc} Nb. In contrast, the absence of intermixing of Ti into Nb layers has been attributed to the increase in the energy of these \textit{bcc} layers with addition of \textit{hcp} Ti. Interestingly, it has
Figure 4.12 Comparison of (a) XEDS and (b) EELS composition profiles of \textit{bcc} Ti/\textit{bcc} Nb multilayer #8.
Figure 4.13 Comparison of (a) EELS composition profile from the present work and (b) Atom probe composition profile of Thompson et al [4] for the $bcc$ Ti/$bcc$ Nb multilayer.
Figure 4.14 Comparison of (a) XEDS and (b) EELS composition profiles of \textit{hcp Ti/bcc Nb} multilayer #10.
been observed here that when the Ti layer has the *hcp* crystal structure, there is essentially no intermixing of Nb into the Ti layers. In this latter case, the addition of *bcc* Nb to *hcp* Ti layers would decrease the stability of the *hcp* phase, and this supports the argument based on thermodynamics. It is noted that in the case of these multilayers with thicker layers, the results obtained from EDS and EELS measurements were similar. Evidently, there is much less excitation of X-rays in adjacent layers in the case of the thicker multilayers.

**4.6.4. Beam broadening issues in composition profiles**

The difference in the XEDS and EELS composition profiles of Ti/Nb multilayers at smaller layer thickness (<3nm) may be attributed to the beam broadening (or spreading) of the fine electron beam in the analyzed volume. The beam broadening due to the elastic and inelastic scattering of incident beam electrons is an important factor affecting the capability of microanalysis and becomes even more critical when there is a need for high spatial resolution on the nanometer scale.

It is possible to predict the amount of electron beam broadening in different materials using models such as Monte Carlo simulations and single scattering approach [7]. Among these, Monte Carlo simulations, which consider not only single scattering events but also multiple elastic scattering events occurring in the interaction volume; yileeds possibly better simulations of the experimental conditions [7,10]. Figure 4.15 (a) is the predicted beam broadening values calculated at various TEM foil thickness using
Figure 4.15 XEDS and EELS (a) Beam broadening vs. TEM specimen thickness in Nb, Cu and Ti and (b) Spatial resolution vs. probe size change in Nb, Cu and Ti at specimen thickness of 120nm.
Monte Carlo simulations for XEDS and simple small angle proportionality for EELS which is:

\[ b \sim \beta t \]  (4.12)

Where \( b \) is beam broadening in nm, \( \beta \) is EELS aperture collection semi-angle in radians and \( t \) is the TEM foil thickness in nanometers.

In this study, the Monte Carlo calculation for X-ray beam broadening was performed based on the method developed by Joy et al \[11\] and a simple small angle approximation was used for EELS calculations \[8\]. Both approaches consider the broadening distance as the radius that contains more than 90% of the scattered intensity. As seen in Figure 4.15 (a), the Monte Carlo calculations indicated an exponential reduction in the beam broadening of Nb, Cu and Ti with reduced sample foil thickness. In contrast, this reduction in beam broadening was linear for EELS with decreasing sample foil thickness. The predicted beam broadening was less for EELS than XEDS for all values of sample thickness.

These calculations might overestimate the absolute values for beam broadening in crystalline materials. The models used for prediction of beam broadening, both for XEDS and EELS, are for elastic scattering in amorphous materials; in the case of crystalline materials, we should expect reduced values for beam broadening due to the effects from the crystalline nature of the materials such as the channeling of the electron beam through the atomic columns. The main advantage of EELS over XEDS is the way that the signal is collected. In EELS there exists a limiting aperture, which defines the
angular range of the signal collected by the spectrometer so that any high angle scattering event is filtered by this aperture.

As can be seen in Figure 4.12 (a), the XEDS results are consistent with intermixing of both elemental species in their neighboring layers. In marked contrast, the results from the use of EELS are consistent with intermixing only of Ti in Nb layers and not *vice versa*. In this way, the EELS results are in complete agreement with those obtained from the comparative technique of the tomographical atom probe as seen in Figure 4.13, whereas the results obtained from XEDS measurements differ. It is believed that this difference between the results obtained from EELS and EDS may be explained by reference to the origin of signals collected by the two different detectors in these techniques. One can also estimate the spatial resolution (R) that can be achieved at given beam broadening and in this case R is given by [7]:

$$R = \frac{d + \sqrt{(b^2 + d^2)}}{2}$$  \hspace{1cm} (4.13)

Where b is the beam broadening and d is the FTHM of the incident electron beam intensity. Equation (4.13) clearly indicates that beam broadening and the FTHM of the probe intensity dominate the achievable X-ray spatial resolution in the microscope. For example, at sample thickness of 120nm changing from a 1nm probe size down to 0.1nm probe size provides approximately 1nm gain in spatial resolution for any element whereas the spatial resolution is better for EELS than XEDS at any given probe size, as shown in Figure 4.15(b).
4.6.5. Composition variations in Cu/Nb multilayer system

An important characteristic of binary Cu/Nb system is the immiscibility between Cu and Nb in the solid state. Although, the room temperature stable form of Cu is $fcc$ and Nb is $bcc$, in the Cu/Nb multilayer system upon reduction of the bilayer thickness, $fcc$ Cu transforms to a pseudomorphic $bcc$ Cu phase. Besides this structural change in Cu/Nb multilayer system, the existence of any compositional variation has been confirmed using complementary analytical techniques. For this purpose, preliminary experiments have been conducted using 3D atom probe analysis and consequently 200 bilayers of Cu and Nb were grown on a Si flat top atom probe specimen substrate at layer thickness of 3nm Cu and 5.5nm Nb. The volume fraction of this film was 0.64 and its bilayer spacing was 8.5nm. For XEDS experiment, the TEM foil was prepared from the same substrate on which the atom probe pillars were deposited for the atom probe experiments. In this way it was possible to compare the XEDS and atom probe composition profiles of the same deposited film.

The growth morphology of the deposited film is represented in the HAADF STEM and bright field TEM images of a cross-sectional sample in Figure 4.16. Figure 4.16 (a) is the HAADF STEM image where the higher atomic number Nb layers appears as bright and Cu are dark. An additional thick Cu protective layer was deposited on top of the multilayers to prevent any possible Ga damage during FIB milling. As expected, the thin film was grown with a textured columnar structure of $<111>$ $bcc$ Nb and $<110>$ $fcc$ Cu along the film normal. The high degree of curvature in the layered structure was due to the conformal roughness developed as the total multilayer thickness has increased.
Figure 4.16 Cross-section view (a) HAADF STEM and (b) Bright field TEM images of the Cu/Nb multilayer, which has also characterized using 3D atom probe microanalysis technique.
The atom probe experiment was conducted on the tip of the sharpened flat top pillars, which were subsequently field evaporated. A characteristic spectrum of the ions was collected based on the mass-to-charge ratio of the elements of the multilayer and this spectrum was further used to construct the 3D distributions of the atoms. Figure 4.17 shows a 3D atom probe reconstruction of a Cu/Nb multilayer consisting of fcc Cu and bcc Nb with thicknesses of 3nm and 5.5nm, respectively. Each individual point in Figure 4.17 (a) and (b) represents an individual atom. The layer thicknesses for the atom probe reconstruction were confirmed by the cross-section TEM measurements. Figure 4.17 (a) and (b) indicates that as compared to the Cu atoms (blue color), the Nb atoms (red color) have significantly interdiffused to the Cu layers. Figure 4.17 (c) shows a composition profile across the Cu/Nb multilayers extracted from the 3D atom probe dataset. This profile indicates ~20-25at% Nb mixing into the Cu layers and ~5at % Cu mixing into the Nb layers. The XEDS experiment was conducted by scanning a fine STEM probe perpendicular to the layers of the same Cu/Nb multilayer and simultaneously acquiring a series of 100 spectra along a 50nm line profile (0.5nm/step). After background subtraction, the intensity profiles for each element were constructed by integrating a 1keV window over the Cu K\(_\alpha\) and Nb K\(_\alpha\) peak intensities. The composition profiles of Nb and Cu were calculated from these integrated intensity profiles using the Cliff-Lorimer equation (eq.4.6) and corresponding k-factor of 0.40 from Table 4.2 for the Cu/Nb multilayer system. Figure 4.18 is the comparison of the XEDS and atom probe composition profiles at layer thicknesses of 3nm Cu and 5.5nm Nb along with an EELS composition profile acquired from Cu/Nb multilayer #11 at layer thickness of
Figure 4.17 3D atom probe reconstructions of (a) Cu ions in blue color (b) Nb ions in red color and (c) Composition profile of the reconstructed fcc Cu/ bcc Nb multilayer.
Figure 4.18 Comparison of (a) Atom probe composition profile (b) XEDS composition profile and (c) EELS composition profile of fcc Cu/ bcc Nb multilayer.
3.7nm Cu and 5nm Nb. First of all, overall composition variation is more flat topped and bottomed in both atom probe and EELS profiles than the XEDS profile in conjunction with a relatively sharper interface along the layers, which was also observed previously in high-resolution HAADF STEM analysis of this interface. The resolution of atom probe perpendicular to the layers was less than 0.05nm where the step size of XEDS and EELS profiles were 0.5nm/step and 0.6nm/step respectively.

All these three different techniques surprisingly revealed a similar composition variation in the layers and one can easily notice the consistent ~20-25 at % Nb mixing into Cu layers and ~5-10 at % Cu mixing into the Nb layers. The techniques that have been employed process different element specific signals; thus atom probe counts the number of individual atoms with respect to their mass-to-charge ratio, XEDS collects the generated characteristic X-rays intensities and EELS collects the characteristic inelastically scattered electron intensities. Surprisingly, all the composition profiles from these three complementary techniques presented similar composition variation at this length scale of Cu and Nb layers. As seen from these composition profiles of the Cu/Nb multilayer, there is an intermixing between the Cu and Nb layers. These composition variations have significant effect on the volumetric free energy change, \( \Delta G \) and eventually on the accurately determination of the interfacial free energy change, \( \Delta \gamma \). Therefore it is necessary to systematically probe the composition changes as a function of individual layer thickness in Cu/Nb multilayer system. Figure 4.19 is the Cu/Nb biphase diagram showing the locations of the multilayers that have been compositionally profiled and their corresponding layer thickness and volume fractions. It should be noted that the technique of choice was EELS, as there exist issues involving beam broadening when
Figure 4.19 Cu/Nb biphase diagram representing the layer thickness and volume fractions of the Cu/Nb multilayers that have been composition profiled and their location in the biphase diagram.
using XEDS at smaller layer thicknesses. All the Cu/Nb multilayers for microanalysis have been selected from the Nb rich side of the biphase diagram. The Nb layer thicknesses were thicker than the Cu layer thickness for all profiles.

Figure 4.20 shows the comparison of the EELS composition profiles of the multilayers Cu/Nb #2 and Cu/Nb#7 at layer thickness of 7.2nm Cu and 12nm Nb for the multilayer #2 and 1.2nm Cu and 3.2nm Nb for the multilayer #7, respectively. The stable phases at these volume fractions and bilayer thickness are \textit{fcc} Cu and \textit{bcc} Nb for Cu/Nb#2 and \textit{fcc/bcc} and \textit{bcc/bcc} for Cu/Nb#7 since it is located at a biphase boundary. As seen in Figure 4.20(a), the composition profile of Cu/Nb multilayer #2 shows a consistent ~5at\% Nb intermixing into the Cu layers whereas it is quite difficult to determine the degree of Cu mixing into the Nb layers due to the extensive compositional oscillations in the Nb layers. The reason for such oscillations in Nb layers thought to be related to a reduction in the Cu signal (i.e. counts) down to a noise level of the spectrometer after the background subtraction. Therefore, it might be assumed that the Cu intermixing into the Nb layers is less than the Nb intermixing into the Cu layers at this layer thickness. Figure 4.20 (b) shows the EELS composition profile of Cu/Nb multilayer #7 at the layer thickness of 1.2nm Cu and 3.2nm Nb. Since this multilayer is located at the biphase boundary it shows a \textit{fcc Cu/bcc} Nb and \textit{bcc Cu/bcc} Nb structure, which was also confirmed by the XRD and HAADF STEM imaging of this sample. The EELS composition profile in Figure 4.20 (b) indicated about 35-40at\% Nb intermixing into the Cu layers and ~5-10at\% Cu intermixing into the Nb layers. It is clear from this composition profile that the amount of Nb intermixing into the Cu layers is significantly increased at reduced Cu layer thickness whereas the amount of Cu intermixing into the
Figure 4.20 EELS composition profiles of Cu/Nb multilayer (a) #2 at layer thickness of 7.2nm Cu and 12nm Nb and (b) #7 at layer thickness of 1.2nm Cu and 3.2nm Nb.
Nb layers slightly increase to ~5-10at%. These results, when considered with the previous atom probe and XEDS composition profiles of Cu/Nb multilayers, indicates that there is an increase in Nb concentration in the Cu layers as the thickness of the Cu layers are reduced. This variation in the concentration of Nb in the Cu layers is plotted in Figure 4.21 as a function of the Cu layer thickness and this plot shows the increase in the Nb concentration with decreasing Cu layer thickness. The error bars in the plot represent 20% error in the accuracy of the EELS quantification analysis.

The quantification in EELS strongly depends on the thickness of the analyzed volume, which can be monitored by the ratio of the first plasmon peak height to the zero-loss peak height ($I_p/I_o$) in the low energy-loss part of the EELS spectrum. The percent deviation of the elemental ratio with the change in plasmon ratio often reflects the thickness contribution of EELS to the employed quantification analysis. In present case an experimental plasmon ratio of $\leq 0.2$ in all EELS profiles results in a corresponding 20% deviation from the true elemental composition ratios [7,8].

4.7. Layer thickness determination in nanoscale metallic multilayers

In metallic multilayers pseudomorphic transformations often occur at the nanoscale régime. Thus, the validity of the classical thermodynamic model in predicting these transformations strongly depends on the accuracy and precision of the dimensions measured at this length scale. The majority of the metastable structures reported in the literature are formed at individual layer thickness of $\leq 2$nm.
Figure 4.21 Nb concentration in Cu as a function of Cu layer thickness.
Sputtering is the common technique in depositing these metallic multilayers and careful calibration of the sputtering system ensures the control in the morphology and thickness of these layers. The rate of the sputtering determines the thickness of the deposited individual layer and consequently the phase of the layer. Figure 4.22 (a) shows a plot of the measured sputtering rate versus sputtering power for Cu and Nb films. The sputtering rates shown in this plot were calculated by measuring the layer thickness from the full width half maximum (FWHM) of the intensity profiles acquired in HAADF STEM images. This process is schematically illustrated in Figure 4.22 (b) for the measurements of Ti and Nb individual layer thicknesses and bilayer thickness of \textit{bcc} Ti/\textit{bcc} Nb multilayer.

Figure 4.22 (a) clearly indicates that for a fixed sputtering pressure (2-4mTorr) the sputtering rates increase linearly with increasing sputtering power. This suggests that for a given sputtering power, pressure, and time, it should be possible to predict the deposited layer thickness using the sputtering rates of a well-calibrated deposition system. Table 4.3 shows the comparison of the layer thickness measured using HAADF STEM intensity profiles, EELS composition profiles and also predicted thickness values using the linear dependency of sputtering rates on the sputtering power. The layer thicknesses from EELS composition profiles were measured by setting the interface between the layer A and B as the point, where the composition of the constituent layers reached 50at%. In general, Table 4.3 shows a good agreement between the predicted layer thickness and layer thickness values measured from HAADF intensity profiles and EELS composition profiles for the stable and pseudomorphic forms of Cu and Ti.
Figure 4.22 (a) Linear increase in sputtering rate for Cu and Nb with increasing sputtering power at constant pressure (2-4mTorr) (b) Illustration of the layer and bilayer thickness measurement using HAADF STEM intensity profile for bcc Ti/ bcc Nb multilayer.
<table>
<thead>
<tr>
<th>Multilayer</th>
<th>STEM HAADF</th>
<th>STEM EELS</th>
<th>Estimated</th>
</tr>
</thead>
<tbody>
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<td>12</td>
<td>7</td>
</tr>
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<tr>
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<td>3.2</td>
<td>1.1</td>
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</table>

<table>
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<th>STEM HAADF</th>
<th>STEM EELS</th>
<th>Estimated</th>
</tr>
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<td>2</td>
</tr>
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<td>Ti/Nb #8</td>
<td>1.8</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Ti/Nb #10</td>
<td>7</td>
<td>9</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 4.3 Comparison of the estimated layer thickness and layer thickness measured using HAADF STEM intensity profiles and EELS composition profiles (Av: Average value).
The agreement in the measured layer thickness values using two different scattering mechanisms, i.e. high angle elastic scattering for HAADF and inelastic scattering for EELS, is within 1nm. The measured sputtering rate for Ti at 100W sputtering power was approximately 0.055nm/sec.

4.8. Predicting phase stability in metallic multilayers

The classical thermodynamic model predicts the phase stability in metallic multilayers through the competition between the bulk and interfacial free energies for two degrees of freedom, bilayer thickness and volume fraction of the each constituent layers. Therefore, the most important thermodynamic variables are the bulk and interfacial free energies, which depend on structural and chemical properties of the multilayers.

In order to establish the thermodynamics of these structural transformations, the properties of Ti/Nb, Cu/Nb and Co/Cr metallic multilayer systems have been considered. The composition and structure changes in the Ti/Nb and Cu/Nb multilayer systems have already been addressed in the previous sections. In addition to these two systems, the biphase diagrams has been successfully applied to modeling the phase stability in Co/Cr multilayers whereas the transformation of stable hcp Co to pseudomorphic bcc Co has been reported upon reducing the individual Co layer thickness to 1.5nm [2,16,17]. Figure 4.23 shows the Co/Cr biphase diagram plotted by using the experimental points from two different references as a function of bilayer thickness, $\lambda$, and volume fraction of Cr, $f_{Cr}$ [16,17].
Figure 4.23  The biphase diagram for the Co/Cr multilayer system [2].
In equilibrium systems, it is common to consider the thermodynamics of the system while defining the concentration range of the phases formed. In this way not only the stability regions of the phases but also the change in the volumetric free energy of the phases can be easily addressed depending on the composition variation of the each component. However, the details of the phase formation still remain effected by the preparation method used. A regular solid solution approach (PANDAT) has been employed to compute the concentration dependency of the Gibbs free energies and eventually the volumetric free energy change between the fcc, hcp and bcc phases has been established (The details of the Cu/Nb database construction were discussed in elsewhere [12]).

Figure 4.24 (a) and (b) show the room temperature volumetric free energy changes for both fcc Cu and hcp Ti with varying Nb concentration and hcp Co with varying Cr concentration, as calculated using PANDAT software. The volumetric free energy change for Cu in Figure 4.23 (a) indicates that up to 55 at% Nb concentration, stable phase is fcc and beyond this point stable phase is bcc. At approximately 40 at% Nb, Cu would not be completely driven to bcc Cu however would have a sufficient reduction in $\Delta G_{\text{Cu}}$. The refined volumetric free energy change at Cu- 40 at% Nb composition is given by $\Delta G_{\text{Cu-40Nb}} \approx 3 \times 10^8 \text{ J/m}^3$. The volumetric free energy change for Ti with varying Nb content reveals that at 15 at% Nb, stable form of Ti is hcp and at this composition, $\Delta G_{\text{Ti-15Nb}} \approx 1.5 \times 10^8 \text{ J/m}^3$. The concentration of Cr in Co was estimated from the argument reported by Boher et al for the Co/Cr multilayers [16]. The authors measured the reduction in the magnetic moment of Co with reducing Co layer thickness (<1.5nm) and at thickness of 0.7nm bcc Co becomes non-magnetic. From this result, they
Figure 4.24 Equilibrium volumetric free energy changes of (a) Ti and Cu with Nb at % concentration and (b) Co with Cr at% concentration.
estimated the Cr concentration as ~25at% in Co, since CoCr alloy becomes non-magnetic at this composition [16]. In addition to this, a significant change in the saturation moment of CoCr alloy thin films has been reported in the 13-25at% Cr concentration in Co range [18]. The Co-13-25at%Cr composition range was used for calculating the volumetric free energy change of hcp Co. Figure 4.24 (b) is the volumetric free energy change of hcp Co with Cr concentration and between 13-25at% Cr composition range, $\Delta G_{\text{Co-13-25Cr}}$ is calculated as $1-1.2 \times 10^8 \text{ J/m}^3$. The slope of the biphase diagrams and the modified $\Delta G$ values were used in estimating the interfacial energy reduction in the metallic multilayers. Table 4.4 lists the volumetric free energies, slopes of the biphase boundaries, calculated interfacial free energy changes and critical layer thickness for the pseudomorphpic phases of bcc Cu, bcc Ti and bcc Co. Using $\Delta G_{\text{Cu-40Nb}} \approx 3 \times 10^8 \text{ J/m}^3$ for the Cu/Nb multilayer system, the interfacial free energy change $\Delta \gamma_{\text{bcc/bcc}}$ was calculated as $-180 \text{ mJ/m}^2$. This estimated interfacial free energy reduction of $-180 \text{ mJ/m}^2$ for fcc Cu to bcc Cu transformation is larger than the reduction of $-141 \text{ mJ/m}^2$ value for hcp Ti to bcc Ti transformation. On the other hand, using the $\Delta G_{\text{Co-13-25Cr}}$ of $1-1.2 \times 10^8 \text{ J/m}^3$, the interfacial free energy change $\Delta \gamma_{\text{bcc/bcc}}$ for the Co/Cr multilayer system was calculated as $-(80-100) \text{ mJ/m}^2$ using the slope of the biphase diagram.

4.9. Discussions on the phase stability of metallic multilayer systems

The formation of a coherent bcc/bcc structure has been demonstrated in the Nb rich part of the Cu/Nb biphase diagram and this result has been confirmed by using plan-view and cross-section characterization techniques. In addition, the atomic structure of fcc Cu/bcc Nb interface at the Kurdjomov – Sachs orientation has been characterized.
Table 4.4 Volumetric free energies, slopes of the biphase boundaries, calculated interfacial free energy changes and critical layer thickness for the pseudomorphic phases of \( bcc \) Cu, \( bcc \) Ti and \( bcc \) Co.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta G , (J/m^3) )</th>
<th>( \Delta \gamma , (mJ/m^2) )</th>
<th>( \Delta \gamma / \Delta G )</th>
<th>( h , (nm) )</th>
<th>Slope, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Nb</td>
<td>3x10^8</td>
<td>-180</td>
<td>0.6</td>
<td>1.2</td>
<td>-0.84</td>
</tr>
<tr>
<td>Ti/Nb</td>
<td>1.5x10^8</td>
<td>-140</td>
<td>0.93</td>
<td>1.88</td>
<td>-0.53</td>
</tr>
<tr>
<td>Co/Cr</td>
<td>1-1.2x10^8</td>
<td>-(80-100)</td>
<td>0.83</td>
<td>1.66</td>
<td>-0.6</td>
</tr>
</tbody>
</table>
The lattice mismatch between the \textit{fcc} Cu and \textit{bcc} Nb in this orientation is 11\%. The HAADF STEM imaging of the \textit{fcc} Cu / \textit{bcc} Nb multilayer has indicated a \textit{semi-coherent} interface decorated by an array of misfit dislocations separated by 6 \{200\} atomic planes whereas the interface between \textit{bcc} Cu and \textit{bcc} Nb was fully \textit{coherent}.

Besides the \textit{bcc} Cu in Cu/Nb multilayer system, the formation of \textit{bcc} Ti in the Ti/Nb multilayer system has been confirmed using HAADF STEM imaging technique. The measured \textit{bcc} Ti layer thickness was 2nm, which was less than the value of 3nm reported by Thompson et al. However, it is interesting note that this value is close to the 1.55nm \textit{bcc} Zr thickness reported by Lowe and Gaballe in Zr/Nb multilayer system [6]. The \textit{bcc} Cu formation has been observed at layer thickness of 1nm in this work and 1.2nm \textit{bcc} Cu was reported by Kung et al [1]. The results of the HAADF STEM imaging have shown that \textit{bcc} Cu was formed at relatively thinner layer thickness than the \textit{bcc} Ti.

The high resolution STEM imaging of the \textit{bcc} Ti/\textit{bcc} Nb multilayer has also revealed a \textit{coherent interface} between \textit{bcc} Ti and \textit{bcc} Nb layers. The orientation relationship between \textit{hcp} Ti and \textit{bcc} Nb reported by Thompson et al was Burgers orientation relationship and the lattice mismatch at this orientation is \(~3\%\). The misfit at the Cu/Nb interface was reduced from 11\% to \(\approx 0\%\) upon transformation of \textit{fcc} Cu to \textit{bcc} Cu. And also, the misfit at Ti/Nb interface was reduced from 3\% to \(\approx 0\%\) upon \textit{hcp} Ti to \textit{bcc} Ti transformation in Ti/Nb multilayers. Therefore, the relative misfit reduction at the interface was greater for Cu/Nb than the Ti/Nb. Surprisingly, the estimated interfacial free energy reduction of \(-180mJ/m^2\) for the \textit{fcc} Cu to \textit{bcc} Cu transformation is larger than the reduction of \(-141mJ/m^2\) value for \textit{hcp} Ti to \textit{bcc} Ti transformation. Since the
misfit between \textit{fcc} Cu/\textit{bcc} Nb multilayers (11\%) is more than \textit{hcp} Ti/\textit{bcc} Nb multilayers (3\%), relatively large reduction in the structural part of the interfacial free energy change for a \textit{semi-coherent fcc} Cu/\textit{bcc} Nb to \textit{coherent bcc} Cu/\textit{bcc} Nb transformation might be expected. It is also very clear from this argument that the reduction in the structural component of the interfacial free energy has driven the transition in both multilayer systems.

Cu and Nb are immiscible and there should be no reaction between the Cu and Nb under equilibrium conditions. However, it is well known from experimental studies that equilibrium process conditions (e.g. epitaxial growth: very low deposition rate and high temperature) are seldom reached in techniques such as magnetron sputtering and physical vapor deposition. Therefore, such processes are widely regarded as being away from or even far from equilibrium [12]. In the literature there have been many example systems reported which are immiscible or have limited equilibrium solid solubility, such as Cu/Co, Cu/W and Cu/Nb, but processed in the form of super-saturated or amorphous alloys using non equilibrium processes [12,13,14,15].

The observed intermixing behavior of the elements with their neighboring layers is somewhat surprising, given the fact that, for both systems Nb has shown greater amount of intermixing into the neighboring layers than vise versa. As seen from the Gibbs free energy curves in Figure 4.25 (a) and (b) pure stable \textit{bcc} Nb has a lower Gibbs free energy than that of Cu and Ti in their unalloyed pure state. Moreover at increasing Cu and Ti concentration, Nb indicates relatively higher positive Gibbs free energy change than that of Cu and Ti suggesting that \textit{bcc} Nb phase is more stable and thus stabilizing or intermixing towards the Cu and Ti layers is thermodynamically more favorable. Figure
4.25 (c) is the Gibbs free energy curve of \textit{hcp-bcc} for Co-Cr multilayer system indicating the change in Gibbs free energies of \textit{hcp} and \textit{bcc} phases with Cr at\% concentration.

From the thermodynamic point of view, as represented in Figure 4.24, both Ti and Cu responds with a reduction in their positive volumetric free energy change for metastable phase formation as the Nb concentration increased. However, this behavior is somewhat different for Cu than Ti. The Ti volumetric free energy reduction is almost linear at all Nb concentrations whereas Cu volumetric free energy does not show a significant reduction up to \(~40\) at\% of Nb concentration in Cu. These arguments suggest that there should be a sufficient reduction in the positive volumetric free energy change of the candidate layer so that the negative interfacial free energy change can successfully drive the pseudomorphic transformation.

The measured interfacial free energy change versus the lattice mismatch (for the Kurdjhomov –Sachs orientation of \textit{fcc/bcc} and Burgers orientation of \textit{hcp/bcc}) of each system is plotted in Figure 4.26. As seen in this plot the measured absolute values for the interfacial free energy change gradually decrease with a reduction in the lattice mismatch and even the Cu/Nb system exhibits the largest driving force to compensate the volumetric free energy increase, \textit{bcc} Ti in Ti/Nb multilayer has shown the largest critical thickness at which the pseudomorphic is stabilized. The competition between the interfacial free energy and the volumetric free energy determines the critical length scale at which the pseudomorphic phase is going to be stabilized.
Figure 4.25 Room temperature Gibbs free energy curves of (a) Cu-Nb system, (b) Ti-Nb system and (c) Co-Cr system.
Figure 4.26 Interfacial free energy change vs. lattice mismatch in different metallic multilayer systems.
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CHAPTER 5

CONCLUSIONS AND FUTURE WORK

The successful applications of aberration correctors have opened up a new era for characterization of nanomaterials in the electron microscope. Achieving a sub-Ångstrom resolution both at parallel and point illumination modes in the transmission electron microscopes (TEM) has revealed exciting performance in terms of materials characterization. Besides the imaging, the corrected electron optics has also enhanced the capability of the STEM based analytical techniques providing smaller (~0.1nm) and brighter electron probes. This improved spatial resolution is very promising and may help to bring the qualitative and quantitative microanalysis in XEDS and EELS down to sub-nanometer scale.

Despite all the advances in the performance of electron microscopes, the high-resolution information transfer is still challenged by the specimen limitations. The samples that are examined in the electron microscopes are often brought to an electron transparency through various ion milling techniques (≥ 5kV), which in most cases alters the surface structure resulting in an amorphous layer and/or defect layer of the material milled. This deleterious surface layer forms a significant fraction of the total sample
thickness and directly affects the quality of the results obtained in the analytical electron microscope.

In this work, low energy Ar ion beam bombardment was used for the removal of damaged surface layers caused by prior high-energy ion milling processes. Consequently, this has resulted significant improvement in the quality of high-resolution imaging of the samples. It is demonstrated that a systematic reduction in the amorphous layer thickness occurs during low energy milling experiments of the Ti6Al4V alloy TEM sample and these results have been confirmed by HRTEM imaging. Several other materials were milled by using low energy Ar ion milling practices (<2kV) and revealed similar improvements in TEM, EFTEM, HRTEM and STEM imaging of the samples.

One of the most important problems in the optics of the modern electron microscopes is the spherical aberration caused by the focusing uncertainty of the electromagnetic lenses. Recently this problem has been solved by the application of the aberration correctors and the resolution of the electron microscope is extended beyond that has been possible in uncorrected microscope. The installation of such corrector on the probe-forming lens of the microscope was successfully done in FEI TITAN 300kV microscope at OSU. Since, we have been characterizing the system and discovering the possible outcomes of the aberration corrected microscopy in characterization of materials at the sub-nanometer and atomic scale.

The preliminary results from the probe corrected FEI TITAN 80-300 S/TEM™ at OSU revealed significant improvements in both imaging and analytical capability of the system. Sub-Angstrom information in the probe corrected mode has been successfully demonstrated in imaging of <110> oriented Si single crystal sample. This fine probe
from the aberration correction has shown further projected benefits on the image contrast and the brightness of the microscope. It has been shown that four times more current in the probe corrected microscope is achievable than in the uncorrected probe at the given spatial resolution (d= 0.12nm). More electrons mean more information from the sample of interest. Overall, aberration corrected microscopy with the combination of analytical techniques such as EELS and XEDS shows a great promise for the characterization of materials at high spatial resolution.

In this present work, these new characterization tools and techniques have been extensively used in efforts understanding the phase stability in metallic nanoscale multilayers. The main concept of phase stability has been established by using a classical thermodynamic model and this model successfully predicted the phase stability in metallic multilayers in cases where the stable phases transformed to a pseudomorphic phase. The classical thermodynamic model depends on the competition between the positive volumetric free energy term and the negative interfacial free energy term in determining the phase stability. One of the important outcomes of the classical thermodynamic approach is the biphase diagram where the stability regions are defined by the biphase boundaries.

In this study, the Nb rich part of the biphase diagram in the Cu/Nb multilayers system has been constructed and the transformation of the fcc Cu to a bcc Cu phase is confirmed. This result is supported using plan-view electron diffraction, reflection XRD and cross section TEM techniques. Since the phase stability of the system relies on the interfacial energies, the structure of the interfaces of both \textit{fcc Cu/bcc Nb} and \textit{bcc Cu/bcc Nb} multilayers have been characterized using HAADF STEM imaging. These results
indicated a semi-coherent fcc Cu/bcc Nb interface to a coherent bcc Cu/bcc Nb interface transformation suggesting that the reduction in interfacial free energy drove the change in phase stability. Similar interface structural transformation was observed in Ti/Nb multilayers whereas upon reduction in layer thickness a coherent bcc Ti /bcc Nb phase was formed.

These structural observations from the nanoscale metallic multilayers were followed by the characterization of the chemical composition as a function of layer thickness in these materials. The high spatial resolution techniques such as Atom probe, STEM XEDS and STEM EELS were employed to detect and measure intermixing. Accordingly, an increased amount of Nb mixing into the Cu layers was observed by reduction in Cu layer thickness. Therefore, the volumetric free energy term was modified considering the compositional change in the Cu/Nb multilayer system.

The modified volumetric free energy changes were used to determine the interfacial free energy changes of both Nb rich parts of the Cu/Nb and Ti/Nb biphase diagrams. These calculated interfacial free energy values are consistent with the structural changes at the interface suggesting a larger misfit reduction for Cu/Nb multilayer than the Ti/Nb multilayer. The observed pseudomorphic layer thickness of bcc Ti was somewhat larger than the bcc Cu and this can be attributed to the difference in the volumetric free energy changes of Cu and Ti where the volumetric free energy change of Cu is relatively larger than that of Ti.

In conclusion, the first applications of newly developed two techniques, focused low energy Ar ion milling and aberration corrected STEM has been successfully demonstrated and with the help of these techniques the phase stability in Cu/Nb
multilayer system in comparison with Ti/Nb multilayer system has been characterized. The classical thermodynamic model explains and predicts these pseudomorphic transitions at the nanoscale. Future work should be aimed at providing a detailed understanding of the intermixing and its effect on different material properties of nanoscale materials such as in the Co/Cr nanoscale metallic multilayers. New techniques such as, low energy Ar ion milling and aberration corrected microscopy can be extensively employed in characterization of bulk and interfaces atomic structures and compositions in wide range of materials.
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