PREDICTING POLYMORPHIC PHASE STABILITY IN MULTILAYERED THIN FILMS

DISSERTATION

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* * * * *

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ABSTRACT

As thin films are reduced in thickness, allotropic phase transformations to structures that are not the equilibrium phase in the standard state can be stabilized. These polymorphic phase transformations have been referred to as pseudomorphism. Many of these pseudomorphic phases have been serendipitously discovered. For the first time, the use of a classical thermodynamic model has been developed in the prediction of phase stability in Zr/Nb and Ti/Nb multilayered thin film structures. Both Zr and Ti exhibit an hcp $\alpha$ to bcc $\beta$ allotropic phase transformation with an increase in temperature. The classical thermodynamic model predicts that in regions of high volume fractions of Nb, the lower volume fraction, or alternatively, the thinner Zr or Ti layer can be stabilized as a bcc phase rather than an hcp phase. A reduction in interfacial energy is sufficient to stabilize this pseudomorphic bcc phase. The classical thermodynamic model also predicts which combinations of length scale and volume fraction will stabilize this phase in a convenient phase stability diagram referred to as a biphase diagram.

The change in hcp to bcc phase stability in Zr and Ti has been confirmed by transmission and reflection x-ray diffraction and electron diffraction. In each case, the Zr or Ti layer adopted a lattice parameter similar to its high temperature $\beta$-bcc lattice parameter. Zr, which has a significant difference in its bcc $\beta$ lattice parameter compared to bcc Nb, became coherent with Nb at a lower thickness after transformation. The addition of this bcc coherency boundary has been added to the Zr/Nb biphase stability diagram. An O-lattice approach and a nearest neighbor bond model have been used to estimate the contributing structural and chemical contributions to Zr/Nb hcp-bcc interfacial energy reduction value.
These values match well to experimentally determined interfacial energies that can be calculated from the slopes of the stability boundaries on the biphase diagram. A van der Merwe interfacial energy model was calculated to compare the interfacial energy reduction between Zr/Nb and Ti/Nb.

The successful prediction of bcc Zr or Ti in volume fraction rich Nb multilayers was used in the prediction and confirmation by x-ray and electron diffraction of a novel bcc to hcp phase stability change for Nb for each multilayer system. The hcp Nb phase has adopted its own independent hcp lattice parameters. In either the Zr/Nb or Ti/Nb system, the hcp Nb lattice parameters were found to be the same. Cross-section electron images indicated a layered structure with morphologically sharp interfaces.

Atom probe tomography of the chemical profile of a Ti/Nb multilayer at the phase stability boundary between hcp Ti to bcc Ti was performed at Oak Ridge National Laboratory. A Matano interface construction of the chemical composition profile revealed diffusivity on the order of $10^{-22}$ cm$^2$/sec. Though this is high for bulk diffusion couples, it is within the diffusivity reported in certain thin film structures. The atom probe analysis indicated that Nb has significantly interdiffused into the Ti layer to a metastable equilibrium concentration of Ti-15at.%Nb. The interdiffusion of Nb into Ti has significantly altered the free energies in stabilizing the bcc Ti phase. Using the atom probe results, the free energy calculations were refined and matched well to predictions using the van der Merwe model.

A series of Ti-8at.%V/Nb multilayers were sputter deposited. The addition of V, a bcc-stabilizer in Ti alloys, has been shown to facilitate the hcp-bcc phase stability in the Ti layer. This result opens up the possibility for predictive phase tuning of multilayers at a specific layer thickness.

Finally, the electrical transport and mechanical properties of the Zr/Nb multilayers were investigated. Changes in phase stability could have a marked influence in the functional properties of these multilayered materials. The superconductivity critical transition temperature, $T_c$, was shown to increase with Nb layer thickness for a constant Zr layer
thickness. Alternatively, the $T_c$ temperature decreased with increasing Zr layer thickness for a constant Nb layer thickness. These changes fit well to existing proximity effect models. The change in phase stability did not appear to alter the transition temperatures suggesting that the Fermi energy levels are relatively the same for the polymorphs. No enhancement of $T_c$ was observed for a reduction in layer thickness for a constant volume fraction indicating that the interfaces are abrupt.

The elastic modulus of the Zr/Nb multilayers was measured by nanoindentation. The values matched reasonably well to values based on a rule of mixture approach. For an extreme Nb-rich coherent $bcc$ Zr / $bcc$ Nb multilayer, an enhancement in the elastic modulus was observed. This is a result of the large elastic strains and extreme layer thickness difference between the two layers that has allowed non-linear elastic modulus anomalies to be detected.

In summary, a series of Zr/Nb and Ti/Nb multilayers have been sputter deposited. A classical thermodynamic model has been used to predict polymorphic phase transitions in each of the constituent layers. Subsequent x-ray and electron diffraction has confirmed these pseudomorphic phases. Modeling has been undertaken to explain the contributing factors for the stabilization of these phases. Additionally, alloying of the Ti layer has shown that engineering phase stability is possible. The functional properties have also been investigated and measured as a function of phase stability.
Dedicated to my family
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CHAPTER 1

THIN FILM GROWTH AND PHASE STABILITY

1.1 Introduction

Thin films, when deposited onto an appropriate substrate at a specific length scale, can exhibit a crystal structure that is different then its equilibrium phase at the standard state of 298 K and 1 atm. This has been referred to as pseudomorphic growth [1]. An example of pseudomorphism is the body-centered-tetragonal (bct) to diamond-cubic phase transition of Sn grown as a thin film on the (001) plane of InSb or CdTe. The diamond-cubic structure is a high temperature phase of Sn [2]. Other observations of high temperature phases being stabilized as thin films at room temperature include hexagonal-closed-packed (hcp) to body-centered-cubic (bcc) Zr in Zr/Nb multilayers [3]. A multilayer is a repeating stack of alternating thin films. In this growth arrangement, the precedent thin film layer can be a template substrate for the proceeding thin film layer. Pseudomorphic phase stability does not always require the stabilization of a high-temperature equilibrium phase. For example, the hcp Co phase can be stabilized as a diamond-cubic phase, which is a non-equilibrium structure on its phase diagram, as a thin film on a GaAs substrate [4]. Additionally, hcp Co
has been stabilized as \textit{bcc} Co in Co / \textit{bcc} Cr multilayers [5] and face-centered-cubic (\textit{fcc}) Co in Co / \textit{fcc} Cu [6] and Co / \textit{fcc} Mn multilayers [7]. Besides Co, other materials have had similar phase stability changes when grown as a thin film including \textit{fcc} Ni to \textit{bcc} Ni in Ni / \textit{bcc} Fe multilayers [8], \textit{bcc} Fe to \textit{fcc} Fe in Fe / \textit{hcp} Ru multilayers [9], and \textit{fcc} Cu to \textit{hcp} Cu in Cu / \textit{fcc} Pd multilayers [10]. For additional pseudomorphic phase stability in other thin film systems, the reader can consult the following references [11-17].

The stability of these pseudomorphic phases has been shown to exist from a few to tens of monolayers in thickness. As thin films in magnetic recording, electronic, and optical properties continue to decrease in thickness to these length scales, marked changes in the functional properties are expected to occur due to the changes in phase stability of these materials. Perjeru \textit{et al.} [49] discussed the phase stability change of \textit{bct} Fe to \textit{hcp} Fe in Fe/Re multilayers. Their results indicated that the \textit{hcp} Fe phase retained its magnetic moment upon transformation. Hunge \textit{et al.} [18] have discussed how \textit{hcp}, \textit{bcc}, and \textit{fcc} phase stability can influence the interpretation of magnetic results. In their work, films of Ni/Fe were deposited. The Ni layer was shown to be \textit{hcp} for 3-6 monolayers. Previous studies had suggested that the Ni grew pseudomorphically \textit{bcc} [19]. The difference in structure alters the interpretation of the magnetic properties for Ni. In another example, Zr has been shown to have a phase stability change from \textit{hcp} to coherent \textit{bcc} in Zr / \textit{bcc} Nb multilayers [3]. Upon transformation the superconductivity transition temperature was reported to have increased. The ability to model, predict, and even engineer phase stability at these length scales is of relevant importance.
Often phase transformations reported in thin films have been serendipitously discovered. This dissertation will discuss, for the first time, the use of classical thermodynamic quantities, in the form of a phase stability diagram, referred to as a biphase diagram [20], in the prediction of pseudomorphic phase stability in Zr/Nb and Ti/Nb multilayers. Chapter 1 provides the framework to the reader on traditional thin film growth and microstructure. A critical review on the current models of polymorphic phase stability is also addressed. Chapter 2 provides the experimental methods for the growth and characterization of the Zr/Nb and Ti/Nb multilayers. Chapter 3 and Chapter 4 are the results and discussion on the phase stability in the Zr/Nb and Ti/Nb multilayers respectively. Chapter 5 addresses phase stability and the functional properties in Zr/Nb multilayers. Finally, Chapter 6 is a conclusion of the findings of this research.

1.2 Thin Film Growth and Microstructure

In the simplest terms, thin film growth occurs by the condensation of atoms on the surface of a substrate. As these adatoms continue to condense and migrate on the surface, a thin solid film grows. The growth of a thin film can be classically described by one of the three different growth modes: The Frank-van der Merwe (F-M) mode, the Volmer-Weber (V-W) mode, and the Stranski-Krastanov (S-K) mode [21]. These modes of growth are illustrated in Fig. 1.1.

To quantitatively describe these modes, a simple case of nucleation with no chemical reactions, alloying, interdiffusion, or changes at the interface will be assumed. In Fig. 1.2 we have a cap shaped nucleus or overgrowth on a substrate with a contact angle $\theta$. The
Fig. 1.1 Representation of the three classical modes of thin film growth on a substrate [21].

Fig. 1.2 Representation of the interfacial energies, $\gamma_i$’s, for an overgrowth, o, on a substrate, s [29].
surface and interfacial energies per unit area are given as $\gamma$ with the subscript $s$, $i$, and $o$ referring to substrate, interface, and overgrowth (film). The resolved forces of the $\gamma$’s are describe in Young’s equation [21] for wetting:

$$\gamma_s = \gamma_i + \gamma_o \cos \theta \tag{1.1}$$

Eq. (1.1) describes the three modes given above in the following manner:

(a) $\theta > 0$ V-W mode and $\gamma_s < \gamma_o + \gamma_i$ (island)

(b) $\theta = 0$ F-M mode and $\gamma_s \geq \gamma_o + \gamma_i$, strain energy small with respect to $\gamma_o$ (layer)

(c) $\theta = 0$ S-K mode and $\gamma_s \geq \gamma_o + \gamma_i$ (layer then island)

In case (a) the overgrowth does not wet the substrate but aggregates into clusters called islands. This occurs when the atoms or molecules in the deposit are strongly bounded to each other than the substrate. This morphology is common for metal growth on insulators, alkali halide crystals, and graphite substrates [22]. Case (b) shows an opposite growth mode of case (a). In the Frank-van der Merwe mode, the film forms a stable nucleus in two dimensions as planar sheets on the substrate. Finally in case (c), the morphology is a combination of case (a) and (b). The film begins to deposit as planar sheets on the substrate, but as it thickens, island growth becomes active. This has been explained as a change in the interfacial energy per unit area of the film [21]. Consider a film grown on a substrate with a lattice constant less then the substrate, i.e. $a_o > a_o^*$. The first monolayer will have its bonds stretched to match the substrate so that $a_{o,1} > a_o^*$ and consequently $\gamma_{0,1} < \gamma_0$ where the subscript 0,1 refers to the film of monolayer one and its layered sequence position from the substrate. Due to the stretched bonds, or greater unit surface area of the film, the surface energy per unit area is decreased for the first monolayer and layer growth becomes favorable. As the
film thickens, each succeeding layer is further removed from the influence of the substrate interface straining the overgrowth bonds, hence $a_{0,1} > a_{0,2} > a_{0,3} > \ldots$ and $\gamma_{0,1} < \gamma_{0,2} < \gamma_{0,3} \ldots$

After the first monolayer, the second layer will have a higher free energy since the area is reduced by a reduction in the stretching of the overgrowth bonds. Once this free energy per unit area is high enough after $n$ layers, layer by layer growth is not favored and island formation begins [22]. From these modes of growth, it is clear that surface energy arguments can be used to describe the morphology of the growth of the film.

Markov and Kaischew [23] expanded upon the surface energy description of growth modes to include crystallographic planes and the influence of supersaturation. In reality, it is clear that the specific orientations of a crystallographic plane will determine the interfacial energy of the surface upon which the film will grow. Furthermore, the rate upon which impinging vapor atoms arrive on the substrate will influence the thermodynamics of the growth. To quantify the latter, supersaturation of the vapor onto the substrate is defined as

$$\zeta = \frac{P}{P_e} = \frac{R}{R_e} = \frac{N}{N_e}$$

where $P$ is the vapor pressure of the impinging species on the substrate and $P_e$ is the equilibrium vapor pressure at that substrate temperature. The $R$'s are the deposition rates and the $N$'s are the adsorbed atom concentration with $e$ referencing the equilibrium condition. Markov and Kaischew [23] considered these influences and rewrote the surface energy as

(a) $\gamma_s < \gamma_{hkl} + \gamma_i - (\Delta \mu / 2k_{bkl}b^2)$, island growth

(b) $\gamma_s \geq \gamma_{hkl} + \gamma_i - (\Delta \mu / 2k_{bkl}b^2)$, layer growth
where $\gamma_{hkl}$ is the specific surface energy of the crystal plane upon which the film grows, $hkl$ are the Miller indices of the plane, $b$ is the nearest-neighbor distance for the substrate, and $k_{hkl}b^2$ is the area of the atom in the contact plane. The $\Delta\mu$ is given as

$$\Delta\mu = kT_s \ln \zeta$$

(1.3)

where $T_s$ is the substrate temperature, $k$ is Boltzmann’s constant, and $\zeta$ is the supersaturation of Eq. (1.2).

Once a nucleus has formed and grown, cluster depletion, seen in Fig. 1.3, can occur through coalescence. During growth coalescence, the shapes of the crystallites can change in a manner that has been described as “liquid-like” [21] even though the substrate temperature is far lower than the melting point of the film material. This process occurs from the rapid diffusion of atoms on the surface driven by the need to minimize the surface free energy [24]. The consequence of growth coalescence is orientation changes of the film and the introduction of defects in the film such as misfit dislocations. Growth coalescence is non-conservative in that a continual adsorption of the vapor atoms to the substrate and/or overgrowth occurs. Once a fixed volume of film is on the surface with no more adsorption of adatoms from the vapor, conservative coalescence can occur in the form of Ostwald ripening or cluster mobility [25-26]. In Ostwald ripening, larger clusters, which may not necessarily be in contact with smaller clusters, grow at the expense of the smaller clusters [27]. This occurs by the surface diffusion of atoms from the smaller clusters to the larger clusters. The degree of Ostwald ripening will depend on the relative binding energies of the migrating atom to the substrate or crystallite compared to the energetics associated with maintaining a smaller cluster size with a larger vapor pressure [21,25]. If the binding energy
**Fig. 1.3** Illustration of the initial stages of thin film growth eventually leading to coalescence of the grains into a polycrystalline continuous film [29].
to the smaller crystallite exceeds that of the substrate, then surface diffusion would not be favored and the smaller cluster atoms may not be depleted. In cluster mobility, the coalescence of multi-atom aggregates occurs by each cluster mutually impacting the other to form a larger cluster. The main observation then is a decrease in cluster density with an increase in mean volume of the clusters [26].

With a semi-quantitative development of early stages of thin film growth discussed, the macroscopic structure of the thin film morphology is developed. As the cluster grows, it can begin to facet and develop a texture [28]. The faceting morphology, hence texture development, is driven by the minimization of the surface energy of the growing planes. An adatom will spend most of its time on an orientation with the lowest potential energy. If this orientation grows the fastest and disappears from the growth form then the adatoms congregate to the next highest energy facet orientation [28]. A crystallite with a small surface area, higher curvature of the facet, will have a higher chemical potential. Therefore, adatoms will tend to migrate and grow on facets with a larger surface area or alternatively a smaller chemical potential [28]. In this manner, the film begins to develop a growth texture or preferred orientation. These features are a function of the surface energies, growth rates of individual facets, and the rate at which the adatoms condenses onto the surface and nucleate for thin film growth. Another critical aspect that can control the texture of a film is a geometric construction known as shadowing [22]. As the growing film develops, facet peaks can prevent the line-of-sight impingement of arriving atoms on the surface. This shadows specific orientations and allows other orientations to grow and develop.
The thin films and multilayers grown in this work were polycrystalline. Each nucleated cluster grew and impinged upon its neighboring grain. As a consequence of the polycrystalline growth, a columnar grain structure resulted from the grain impingement in-plane with continued vertical growth out-of-plane. Even though the film is polycrystalline, epitaxy of individual layers can occur within the columnar grain morphology since a template interface structure has been established between the layers within the columnar grain.

1.3 Epitaxy and Misfit Dislocations

As the overgrowth of the deposit condenses onto a substrate, unique orientation relationships can develop between the film-substrate interface. This has been referred to as epitaxy [30]. In the initial growth of the overlayer, the first few deposited monolayers will typically attach and strain homogeneously to match the substrate lattice spacing $a$. But as the overlayer continues to grow, the atom-atom interactions of the overlayer begins to dominate such that the overlayer prefers its own interparticle spacing of $b$. The competition between these two interparticle spacings is referred to as misfit and is defined as

$$f = (b - a)/b$$  \hspace{1cm} (1.4)

The misfit describes the geometric lattice mismatch between the overgrowth and the substrate. A second parameter, $\mu$, is also used in conjunction with $f$. $\mu$ is the ratio of the overgrowth-substrate atomic interaction strength to the overgrowth-overgrowth atomic interaction strength [1]. This term describes the chemical bonding mismatch at the interface.

Frank and van der Merwe [31] proposed a simple model to illustrate the above concept. They considered a monolayer of foreign atoms on a rigid substrate. These atoms
were one-dimensional and were coupled to each other with harmonic springs. These springs were subject to external sinusoidal potential represented by the substrate. The period of the potential was $a$ and the natural spacing between the atoms as $b$. The spring constant and the potential well depth were determined by $\mu$. If $f$ is small and $\mu$ is not too large, the over layer will strain uniformly to match the lattice constant of the substrate. As the misfit was increased, eventually the lattice mismatch could not be accommodated by uniform strain. At this critical point, $f_c$, a defect, referred to as a discommensuration, appears. A discommensuration is a narrow region where the adatoms are out of registry with the substrate. This can be referred to as a semi-coherent interface. As $f$ continues to increase, the discommensuration decreases and a smooth transition from a commensurate to an incommensurate interface forms.

It has been further pointed out by van der Merwe [32] and Jesser and Kuhlmann-Wilsdorf [33] that as succeeding layers grow upon the initial monolayer, they too will be in a state of uniform stress if the underlying layer is strained into commensurability. They concluded that a critical film thickness, $h_c$, the strain energy for coherency to the layer below it is too large and a discommensuration in the form of a misfit dislocation is inserted at the interface. This defect will then help reduce a fraction of the strain [34]. As the film continues to grow in thickness, the density of interfacial dislocations increases up to a certain critical thickness. At this height, the strain is reduced to zero and the film is no longer coherent to the substrate.
1.4 Pseudomorphism

From the above descriptions, it is quite clear that the film growth process is very dynamical and can generate specific morphological structures and orientations. These growth effects have lead to considerable interest in the types of morphologies, microstructures, and phases that can be processed in a thin film [35-36]. As discussed in Section 1.1, thin films can adopt pseudomorphic phases different than their bulk equilibrium structures. The adoption of these crystal phases is in response to a lowering the systems total energy. The following models based on coherency strain[1], stacking fault potentials [37], and classical thermodynamics [20], have been developed to explain under which condition pseudomorphic or normal growth can be expected in thin film systems.

1.4.1 Coherency Strained Induced Pseudomorphism

Since an overgrowth can strain via elasticity theory to match the lattice spacing of the substrate, a model based upon coherency strains [1] has been developed to rationalize pseudomorphic phase stability. In the example of Sn in Section 1.1, the transition from a bct to a diamond-cubic is believed to be a result of the Sn reducing the strain that would accompany the bct structure on the (001) InSb or CdTe substrate [12]. Bruinsma and Zangwill have proposed a model [1] that considers the large shear stresses in conjunction with the adhesive forces of the substrate to explain why certain materials undergo structural transitions. In their paper [1], a nonlinear generalization of the Peierls-Nabarro model was adopted. They assumed systems that had the two-dimensional layer-by-layer growth (Frank-van der
Merwe mode) with only one single transition as a function of increasing overgrowth thickness. The authors freely admit this limits the theory for structures that may go through a series of transitions with increasing thickness.

To begin, they considered Cahn’s [38] description of a large stress upon the free energy density of a bulk crystal. Cahn reported that at small strains, the crystal symmetry was always lowered and the energy density of deformation increased with the square of the strain. He also noted that as the strain increased, for specific orientations, a specific symmetry group became appropriate at certain values of strain, \( \varepsilon^* \). At these \( \varepsilon^* \) values, the symmetry was higher then other points along the deformation path but had a local minimum in the free energy density \( f_B \) as ishown in Fig. 1.4. In Fig. 1.4, the stability of the structure is determined by the curvature of \( f_B \). In regions where the curvature is positive, a local minimum is developed and the strained crystal is mechanically stable. In the region between \( \varepsilon^- \) and \( \varepsilon^+ \) the curve is convex and the crystal is mechanically unstable.

Fig. 1.5 is a compilation of Bruinsma and Zangwill’s results [1] for a film deformed along an easy direction on a substrate experiencing an interfacial stress of the Peierls-Nabarro type. By combining various plots of \( f_B \) vs. \( \varepsilon \) (Fig. 1.4), two cases were considered: a strong adhered substrate (\( \mu >> 1 \)) and a weak adhered substrate (\( \mu << 1 \)). In the phase diagram of Fig. 1.5, the film thickness height, \( h \), and the mismatch, \( f \), were plotted. Recall that \( f_B \) is an energy density whose volume is the film’s surface area multiplied by the film’s height \( h \). This allows \( h \) to be a constant multiplication scaling factor since the area of the film is fixed. In Fig. 1.5(a), the strong adhesion case is plotted. Monolayer films are strained into commensurability for all misfits. The authors further state that the critical height, \( h_c \), where
**Fig. 1.4** The change in the free energy function, $f_B$, for a material with strain, $\varepsilon$. Local minimums may exist along the free energy curve for specific values of strain, $\varepsilon^*$. These minimums in free energy correspond to pseudomorphic phases structures [1].

**Fig. 1.5** Structural phase diagram as a function of film height, $h$, and misfit, $f$. Case (a) strong film-substrate adhesion. Case (b) weak substrate-film adhesion [1].
a coherent-incoherent transition occurs, is proportional to the inverse of misfit, i.e. \( 1/f \). As \( f = f^- \) (and \( f \equiv \varepsilon \)) is approached, a uniformly strained overlayer is unstable, i.e. regions near \( \varepsilon^- \) on Fig. 1.4. In the region between \( f^- \) and \( f^+ \), the coherent-incoherent transitions are triggered by an instability towards a modulated structure of the two phases analogous to spinodal decomposition. Mechanical stability is recovered for misfits in excess of \( f^+ \) because the metastable structure has the lowest free energy for a thickness less than \( h_c \). As the film thickness increases beyond this value, a martensitic transformation occurs from an incoherent pseudomorphous phase to an incoherent bulk stable phase.

In the case of a weakly bonded overgrowth in Fig. 1.5(b), the theory predicts that the layers will be incommensurate. Since the film is weakly bonded to the substrate, large elastic strains to match the substrate would not be expected. Experimentally, it would be more probable that a weakly bonded film would growth with the three-dimensional Volmer-Weber growth mode instead of the planar sheets of the Frank-van der Merwe mode as assumed by this coherency model. The weak surface bonds are insufficient to counterbalance the force of the overgrowth’s tension and misfit strain with the substrate.

In review, Bruinsma and Zangwill’s theory [1] is only applicable to systems of a single overgrowth. It provides an explanation to why a transition can occur and the pseudomorphous symmetry formed by that transition from the calculations of \( f_B \). Unfortunately a detailed knowledge of \( f_B \) may not be readily available for predicting and modeling these phase transformations. The response of \( f_B \) to a specific strain is substrate dependent and is not applicable for a general description of phase stability. The model fails to predict multiple
transitions with increasing thickness as pointed out by the authors. Multilayered films have been reported to undergo multiple transitions within the stacking sequence [20].

1.4.2 Redfield-Zangwell Model of Stacking Faults

The Redfield-Zangwell model was proposed to describe structural transitions in closed packed metal multilayers, i.e. hcp and fcc [37]. It is well known that a fcc stacking of ABCABC... , where A, B, and C refer to atomic layering sites, can be transformed to a stacking of ABAB... by the introduction of intrinsic stacking faults [39]. The electronic oscillatory interaction between the closed-packed planes of these two stacking structures is derived from Friedel oscillations [40]. Friedel oscillations are decaying oscillatory functions associated with the electronic potential within the material [41]. Redfield and Zangwill expanded upon the concept of Friedel oscillations to explain the unusual stacking sequences reported in metallic multilayers of hcp and fcc layering.

The theory [37] assumes a tight-binding model of a metal with only second nearest neighbor interactions. It considers the second nearest neighbor potential change, ΔV, if a defect layer is inserted between two successive layers. In their notation, layers with identical neighbors are denoted as h and layers with planes of different nearest neighbors on either side are denoted as c. Thus an hcp metal is hhh... and a fcc metal is ccc... in the closed packed directions. The model also has a term, ΔF, associated for two different crystals being brought together. The ΔF stands for the difference in bandwidths, band fillings, interfacial bonding, or a combination of these that would be expected if two different metals
are in contact at an interface. With these two terms, the change in energy, \( \mu(d) \), of a stacking fault placed a distance \( d \) from the interface is given as

\[
\mu(d) = \mu_b + \Delta F \cdot \Delta V \cdot B(E_F) \cdot \sin\left\{ 2d \cos^{-1}\left[ \frac{(E_F/6V')} + 1 \right] + \delta \right\} / d^2
\]

(1.5)

where \( \mu_b \) is the bulk stacking fault energy, \( d \) is in units of the interplanar spacing, \( E_F \) is the Fermi energy level, \( B(E_F) \) is a slowly varying function of band occupancy, \( V' \) is the nearest neighbor hopping integral, and \( \delta \) is a phase shift. This equation can be rewritten as

\[
\mu(d) = \mu_b + \Delta F \cdot \Delta V \cdot B(E_F) \cdot \sin\left\{ 2\pi d / \lambda_F + \delta \right\} / d^2
\]

(1.6)

where

\[
\lambda_F = \pi / \cos^{-1}\left[ \left( E_F / 6V' \right) + 1 \right]
\]

(1.7)

The key point of Eq. (1.6) is that a Friedel-like oscillatory modulation, \( \lambda_F \), to the bulk equilibrium stacking fault chemical potential occurs with the introduction of a bicrystal interface. Fig. 1.6 is a plot of the oscillation due to the stacking fault energy as a function of distance from the interface. In a system of a series of bimetallic interfaces, the atomic planes within each layer will feel the effect of two oscillatory potentials, one from each bounding interface. The stacking sequence is determined by the superposition of these oscillatory potentials. The amount of stacking faults in a layer therefore is the phase difference between the two bounding oscillations whose modulations are a function of layer thickness. If the two waves are out-of-phase, destructive interference occurs and bulk structures dominant. This is seen for a layer thickness \( >\lambda_F \) and \( <\lambda_F \). If the modulations are in phase and of the order of \( \lambda_F \), a non-bulk equilibrium stacking sequence occurs for that material.

This model has been successfully used to explain some of the structural transitions seen in the Al/Ti multilayers [42]. The Al/Ti multilayer, depending upon the length scale of
Fig. 1.6 A plot of the oscillations of the stacking fault energy as a function of distance from the interface [37].
each of the constituent layers, can undergo a $hcp$ to $fcc$ transition in Ti or a $fcc$ to $hcp$ transition in Al. Banerjee [42] has reported that the $\lambda_p$ for $fcc$ Ti phase stability would be in the range of 10.5 nm to 4.9 nm (45 to 20 closed packed atomic planes). The Al transition to $hcp$ is in the range of 4.9 nm to 2.6 nm (21 to 11 closed packed atomic planes). These results match the experimentally observed transitions for the 10 nm / 10 nm, 5 nm / 5 nm, and 2.5 nm / 2.5 nm films.

Banerjee [42] also noted the inconsistencies with the Redfield-Zangwill model for the following Al/Ti multilayers cases: For a 5 nm Ti layer, the model predicts that this layer is less then the $\lambda_p$, and therefore Ti should have an $fcc$ stacking. When the Ti thickness is 2.5 nm, it is sufficiently less then Ti’s $\lambda_p$ and $hcp$ stacking should be stabilized. As stated above, the 5 nm Ti layer in a 5 nm / 5 nm multilayer exhibited $fcc$ stacking and in the 2.5 nm Ti layer in 2.5 nm / 2.5 nm multilayer $hcp$ stacking is observed. These results are consistent with the model. But if the multilayer is 2 nm Al / 5 nm Ti, $hcp$ stacking is observed and in a 5 nm Al / 2.5 nm Ti multilayer, $fcc$ stacking is reported. These results are inconsistent with the predicted stacking sequence of the Ti layer.

The model inherently treats the transitions in each layer independent of each other [43]. The model is unable to clearly predict transitions that occur for differences in the volume fraction of Ti, $f_{Ti}$, for the bicrystal. Furthermore, the model is based on a tightly bounded (or a nearly free-electron type) metal. This is a good approximation for Al but may not be for Ti, a transition metal whose d orbitals play a significant role in bonding. The model is designed for only closed packed stacking sequences which limits its applicability.
Though this model is a good first approximation for determining structural transitions, a more generalized approach needs to be established that could have applicability to all systems.

1.4.3 Phase Stability in Classical Thermodynamics

The stability of a phase when viewed from a classical thermodynamics perspective is based upon a balance between the interfacial free energy and volume free energy of each phase which are in contact with each other [36]. Pseudomorphic phases can be formed and stabilized by the competition between these two energies.

1.4.3.1 Single Film on Substrate

In the work by Jesser [44], pseudomorphic growth was described in terms of the initial stages of nuclei formation. Consider two phases, \( \alpha \), which is the bulk equilibrium phase, and \( \alpha' \), which is the pseudomorphic phase. In Jesser’s work [44], the interfacial energy of \( \alpha' \), \( \gamma_{\alpha'} \), is less than that of the interfacial energy of \( \alpha \), \( \gamma_{\alpha} \), on the substrate. From Eqs. (1.2) and (1.3) in Section 1.2, the free energy of the nucleated overgrowth is a function of the vapor pressure to the equilibrium vapor pressure of the condensed phase. Under typical vacuum deposition conditions for thin films, there exists a sufficiently high vapor pressure or alternatively a low substrate temperature such that the chemical potentials of \( \alpha \) and \( \alpha' \) are approximately equal. Since the interfacial energy of \( \alpha' \) is lower, nucleation theory predicts that the pseudomorphic nuclei formation rate is greater than that of the bulk equilibrium phase [44].
Eventually, a critical radius will be approached beyond which the pseudomorphic growth is energetically favorable. The nuclei will then transform to the bulk equilibrium phase. This critical transformation radius can be found by considering the total Gibbs free energy difference, $\Delta G_I$, between the two systems for $\alpha'$ and $\alpha$ on the substrate. It is given as

$$\Delta G_I = \Delta G_\alpha - \Delta G_\alpha' = A_i (\gamma_\alpha - \gamma_\alpha') + A_o (\gamma_\alpha' - \gamma_\alpha) + V_o \Delta G_v + E_\alpha - E_\alpha'$$

where $A_i$ is the interfacial area in contact with the overgrowth, $A_o$ is the overgrowth area not in contact at the interface, $V_o$ is the total volume of the overgrowth, $\Delta G_v$ is the volumetric free energy difference between bulk $\alpha'$ and $\alpha$ phases, and $E$ is the total elastic strain. By properly defining the area and volume of the overgrowth in terms of the radial size of the overgrowth, $\delta\Delta G_I/\delta r = 0$ can be used to find the critical radius, $r^*$ for nuclei growth.

Eq. (1.8) can be simplified if we assume the overgrowth to be a continuous planar surface. This is equivalent to the pseudomorphic phase’s nuclei impinged upon each other and can only increase in volume by growing in one direction, out-of-plane. In this treatment, we do not consider the early stages of nucleation and growth. This is a valid assumption for the purposes of this topic in that we are interested in the layer thickness range that favors pseudomorphic phase stability. For simplicity, all terms that scale with volume will be included in the volumetric free energy term, $\Delta G_v$, and all terms that scale with area are included in the interfacial free energy term, $\Delta \gamma$. The $\Delta$ references the difference in free energy between the pseudomorphic and bulk equilibrium states prior to and subsequent to the transformation. The total Gibbs free energy difference, $\Delta G_I$, is re-written as

$$\Delta G_I = (\Delta G_v) (At) + \Delta \gamma (A)$$

(1.9)
where $A$ is the surface area of the film and $t$ is the thickness of the film. While the volumetric free energy will be positive, the change in interfacial free energy will be negative. Therefore, $\Delta \gamma$ ($< 0$) is the thermodynamic driving force for stabilization of the pseudomorphic phase as correctly pointed out by Jesser [44]. The critical thickness for transformation to the bulk equilibrium structure is given as

$$t_{\text{critical}} = -\frac{\Delta G_v}{\Delta \gamma}$$  \hspace{1cm} (1.10)

and can be simply derived from Eq. (1.9). In this expression, the film has a single degree of freedom, $t$, in stabilizing the pseudomorphic phase. Recently Herr [45-46] has described amorphous to crystallization in Fe(Zr) alloy films as a function of these thermodynamic quantities.

1.4.3.2 Multilayered Thin Films

Unlike a single film on substrate, a multilayered thin film comprising of A/B alternating layers has an additional degree of freedom [20]. Dregia et al. [20] properly extended the thermodynamics to account for this addition in the thermodynamic framework of multilayered thin films. The two independent degrees of freedom are the length scale given as the sum of layer A plus layer B (referred to as the bilayer thickness, $\lambda$) and the volume fraction, $f_i$, of A or B for the multilayer. Note that the volume fraction of A or B can be written in terms of the other since

$$f_A + f_B = 1$$  \hspace{1cm} (1.11)

The entire stack of A/B layers can be represented energetically as an unit bilayer comprising of layer A, layer B, and two A/B interfaces. This unit bilayer is illustrated in Fig. 1.7. The
Fig. 1.7 A unit bilayer that defines the energetic framework of the A/B multilayer stack
The bilayer’s total free energy is then

\[ G = N_A \mu_A + N_B \mu_B + 2 \gamma A \]  \hspace{1cm} (1.12)

where \( N_i \) is the number of atoms of species \( i \), \( \mu_i \) is the chemical potential of \( i \), \( \gamma \) is the interfacial free energy between A and B, and \( A \) is the area of the interface. In this model, each previous layered surface acts as a template layer for the next layer. In this approach, the rigid substrate will be assumed to have little to no influence on the multilayered film growth. In the experimental work reported in this dissertation, the films were deposited onto an amorphous oxide or native oxide surface to prevent crystallographic coherency strains within the film from the substrate and prevent any crystallographic orientation relationship to develop between the substrate and film. It will be further assumed that the coherency strains between the layered films are negligible. The influence of coherency strain will be applied to the model as a separate quantity in subsequent sections.

In Eq. (1.12), the interfacial area is a constant within a multilayer since the planar growth is fixed by the substrate and the vertical growth direction can be adjusted. If this was not the case, the multilayer system would vary to find an equilibrium shape with the minimization of the interfacial area [20].

If we consider a multilayer in which at least one of the layers has been transformed to a pseudomorphic state, the free energy of Eq. (1.12) would then be given as

\[ G’ = N_A \mu_A’ + N_B \mu_B’ + 2 \gamma’ A \]  \hspace{1cm} (1.13)

The primes refer to the new energetic states of the pseudomorphic phases. In each case, the area is fixed as discussed above and can be used to normalize the thermodynamic terms for the entire system. The adjustable vertical growth direction is then defined as the bilayer, \( \lambda \),
for the two multilayers. \( \lambda \) is given as

\[
\lambda = h_A + h_B
\]

(1.14)

where \( h_i \) refers to the layer thickness of \( i \). The free energy difference between Eq. (1.12) and Eq. (1.13) for an unit bilayer is [20]

\[
\Delta g = 2\Delta \gamma + [\Delta G_A \lambda_A + \Delta G_B \lambda_B] \lambda
\]

(1.12)

where \( \Delta g \) is the normalized to area change in free energy, \( \Delta \gamma \) is the change in interfacial free energy, \( \Delta G_i \) is the allotropic free energy change per unit volume of reference phase metal \( i \), and \( f_i \) is the volume fraction of species of \( i \). Note that the product of \( f_i \cdot \lambda \) is the layer thickness for metal \( i \) in the reference bilayer. Thus the two independent degrees of freedom in \( \lambda \) and \( f_i \) are available to the multilayer to stabilize pseudomorphic phases and are properly accounted in the total thermodynamic energy. These two terms are similar to conventional thermodynamic state variables of pressure and temperature. The equilibrium structure in the bilayer is determined by the lowest specific free energy for the formation of \( \Delta g \) as a function of these two variables. This is depicted in Fig. 1.8.

In Fig. 1.8(a), a free energy line, from Eq. (1.15), is drawn. At a large bilayer thickness, \( \lambda \), the lowest free energy corresponds to the case where both layers’ phases are present in their bulk equilibrium structures. This line, of course, will have zero slope since each material is in its bulk phase (no change in free energy, \( \Delta G_i \)). Once the bilayer is reduced in thickness below a critical thickness, \( \lambda^* \), the pseudomorphic structure of B’ is now the phase with the lowest free energy in combination with the bulk equilibrium phase of A. The phase transition to B’ is driven by the interfacial free energy reduction of the multilayer given as the y-intercept on this graph. The slope of the pseudomorphic free energy line, which intersects the bulk equilibrium A/B free energy line, is \( \Delta G_B \cdot \lambda_B \) and can be simply determined from Eq.
Fig. 1.8 A free energy, $\Delta g$, verses bilayer spacing, $\lambda$, plot taken from the equation of a line [Eq. (1.15)]. (a) At $\lambda < \lambda^*$, the pseudomorphic phase, $A/B'$, has the lower total energy. (b) By changing the volume fraction of $B$, $f_B$, the slope of the free energy line is altered and a new $\lambda^*$ is required to stabilize the pseudomorphic phase of $A/B'$ [20]
(1.15). Since the interfacial free energy reduction and volumetric free energy difference are treated as fixed values, if the volume fraction of component B, \( f_B \), is now increased and fixed for the same bilayer spacing, a new free energy curve in \( \Delta G \) verses \( \lambda \) must be drawn. The influence of this new variation in volume fraction of B causes the slope to increase while reducing the critical thickness for the transition to B’ as illustrated in Fig. 1.8(b). The increased volume fraction (volumetric free energy contribution) reduces the bilayer length scale at which the interfacial free energy can stabilize the B’ phase.

This method of plotting compositional variations and their influences on structural phase stability is cumbersome. A more attractive method is the biphase diagram [20]. An example of the biphase diagram for the A/B and A/B’ phase stability in Fig. 1.8 is presented in Fig. 1.9. 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. The biphase diagram is analogous to traditional metallurgical phase diagrams in which free energy verses compositions at various temperatures are used to plot allotropic phase transformations as a function of temperature verses composition.

In the biphase diagram description, a phase boundary, which is defined by \( \lambda^* \), is a function of \( 1/\lambda \) verses \( f_B \). In this approach a two-phase region that separates the bulk equilibrium phases of A/B from the pseudomorphic phase of A/B’ can be conveniently represented. The slope of this phase stability boundary in Fig. 1.9(a) can be derived from Eq. (1.15) and is given as

\[
slope = m_B^* = -\Delta G_B'/(2\Delta \gamma_B')
\]  

(1.16)
Fig. 1.9 (a) A biphase diagram separating the phase stability region between A/B and A/B'. (b) If phase A can exhibit a pseudomorphic A' phase, the biphase diagram will exhibit a triple point [20]
The slope is positive for the B to B’ example since the free energy differences have been defined to be negative (pseudomorphic free energy minus bulk equilibrium free energy). In Fig. 1.9(a), the boundary has been drawn as a linear line. If coherency strains are included to Eq. (1.15), \( \Delta g \) would be nonlinear and depend upon the volume fraction since coherency strains are inversely proportional to thickness [38]. This influence would lead to curved boundaries on the biphase diagram. At values of \( f_B = 0 \) or \( 1 \), the system is undefined since no interfaces are present. Note that in cases in which component A can transform to a pseudomorphic phase, A’, the biphase diagram can exhibit a triple point, i.e. regions of phase stability for A/B, A'/B, and A/B’. Similarly, the slope that separates the A/B and A'/B phase field for this diagram would be given as

\[
\text{slope} = m_{A'} = \Delta G_A/(2\Delta \gamma_{A'})
\]

(1.17)

and the slope of the phase stability boundary separating the A'/B and A/B’ phase fields is determined by the difference in slope of the other two boundaries, i.e. Eqs. (1.16) and (1.17).

Fig. 1.9(b) is a biphase diagram in which each layer in the multilayer exhibits a pseudomorphic phase depending upon the length scale and volume fraction of B.

**1.4.3.3 Applicability of the Biphase Diagram**

The experimental value of the biphase diagram is its ease of use in predicting which combinations of length scale and volume fractions will result in pseudomorphic phase stability. It has been successfully applied to modeling the phase stability in Co/Cr multilayers [20]. Phase transformations in both the Co and Cr layers has resulted in considerable confusion for this system. One group of researchers has reported a phase stability change in
Co from \textit{hcp} to \textit{bcc} \cite{5} while another group has reported a phase stability change in Cr from \textit{bcc} to \textit{hcp} \cite{47}. The phase stability discrepancy between the two groups has resulted in considerable controversy \cite{5}. By plotting the experimental points from each group as a function of bilayer thickness, $\lambda$, and volume fraction of Cr, $f_{\text{Cr}}$, an experimentally determined biphase diagram for Co/Cr can be seen in Fig. 1.10. By viewing the phase stability from a classical thermodynamic perspective of the biphase diagram, the controversy for these transitions can be understood. Each research group grew their multilayers with a different volume fraction though the bilayer thickness was nearly identical. As discussed previously, the volume fraction of material alters the length scale at which the interfacial energy can stabilize the pseudomorphic phase. In typical pseudomorphic transformations, the transformed Cr layers have adopted a similar crystallographic phase (similar symmetry) as the template layer beneath it. The biphase diagram provides a visual tool in recognizing when and where specific transitions occur.

The slopes of the boundaries in Fig. 1.10 were used to estimate the interfacial free energy reduction for the phase stability changes. Using CALPHAD calculated volumetric free energy differences in the literature \cite{48}, along with the measured slopes, the interfacial free energy reduction were found to be $\Delta\gamma_{\text{hcp/hcp}} = -356$ mJ/m$^2$ and $\Delta\gamma_{\text{bcc/bcc}} = -537$ mJ/m$^2$ respectively \cite{20}. These values are on the order of typical incoherent or semi-coherent solid/solid interfacial energies. This would suggest negligible influence of coherency strains in driving the transformation and allow for linear boundaries on the biphase diagram to be plotted.
Fig. 1.10 The applicability of the biphase diagram resolving the confusion over which constituent layer transforms to the pseudomorphic phase. The respective research groups [5] and [47] were depositing multilayers in different regions of the biphase diagram [20]
1.5 Summary

The growth of thin film materials is well understood and established. Three modes of growth have been described, Frank-van der Merwe, Volmer-Weber, and Stranski-Krastanov. The determination of which mode is to occur is a function of the interfacial energies of the under- and over-layered materials. But the determination of the crystal structure of which the deposited overlayer forms is still relatively primitive. In many cases, this crystallography is one that is pseudomorphic for the overgrowth. The formation and stability of these pseudomorphic phases has been categorized into coherency strain induced transitions, the Redfield-Zangwill model, and classical thermodynamics. These categories have been discussed in detail above. Of the three, the classical thermodynamics has developed a clear and convenient biphase diagram to illustrate where these transitions occur. The use of the biphase diagram, in Chapter 3 and Chapter 4, in predicting and confirming phase stability in Zr/Nb and Ti/Nb multilayers is the focus of this research.
References for Chapter 1


CHAPTER 2

EXPERIMENTAL METHODS

2.1 Physical Vapor Deposition

Thin films can be grown through a variety of techniques including Chemical Vapor Deposition (CVD) [1] and Physical Vapor Deposition (PVD) [1]. PVD generically refers to the process in which a material goes from a condensed phase to a vapor phase and back to a thin film condensed phase. Most, if not all, of these processes occur in a vacuum. This is done to allow for increased mean-free-path transfer of the vapor to the substrate, a reduction of atmospheric contamination within the film, and a low-pressure environment for the ionization of a working gas [1]. The mean-free-path, $\Gamma$, of an atom in a gaseous environment is given as

$$\lambda = \left(2^{1/2}n\sigma\right)^{-1}$$

(2.1)

where $n$ is the number of molecules per unit volume and $\sigma$ is the cross-sectional area of the gas molecules [2]. As the number of molecules per volume increases (or pressure), the mean-free-path decreases for each atom resulting in more random collisions between the
vapor-phase atoms. These collisions reduce the kinetic energy of the arriving atoms onto the substrate.

The reduction in kinetic energy of these atoms can have substantial influence on the microstructure of the deposited film. Thornton [35] has written extensively how PVD processing variables influence the final microstructure of sputtered deposited films. In this work, a preliminary study on sputtering pressure at ambient deposition temperatures was investigated.

Fig. 2.1(a) is a plot of grain size verses sputtering gas pressure for a series of Nb monolithic films. As the pressure was increased, the in-plane grain size, determined by Transmission Electron Microscopy (TEM), became dramatically smaller. The reduction in the energy of the arriving atoms limited their surface mobility, hence coalesce, on the substrate surface. Coupling the reduced surface mobility to a reduced film thickness has allowed for a significant reduction of the polycrystalline grain size. The reduction in grain size has generated a lattice dilation of the \textit{bcc} Nb lattice parameter. The \textit{bcc} phase (and lattice dilation) was confirmed by x-ray and plan-view diffraction. The lattice dilation, as a function of grain size, is plotted in Fig. 2.1(b). The lattice dilation for the nanocrystalline grains is a result of the size and pressure effects of the grains to the excess free volume of the grain boundaries [36]. To avoid the added complexity of lattice dilation and other nanocrystalline effects, the films in this study were deposited at low sputtering pressures, i.e. 2-4 mTorr, with grains > 15 nm
Fig. 2.1 (a) Grain size verses sputtering power for monolithic Nb thin films. (b) The change in lattice parameter with change in nanocrystalline grain size for Nb.
2.1.1 Sputtering Rates

PVD dc magnetron sputtering was used to deposit the Zr/Nb and Ti/Nb multilayered thin films. The mechanism for sputtering involves the use of a plasma discharge in the removal of atoms from a source material, commonly referred to as a target, to a substrate [1]. Positive ions of a fairly high atomic number, Z, are accelerated to a target surface from a plasma via an electric field. The larger mass of the working gas provides more kinetic energy per accelerating voltage. Argon is a typical working gas for sputtering. The ions collide with the surface, transfer their kinetic energy to the target atoms, and if the energy is sufficient, the surface bonds can be broken and one or more target atoms are released. The sputtering yield is the number of ejected atoms to incident ion.

Fig. 2.2 is a plot of sputtering rate verses sputtering power for a bcc Nb film. The plot indicates that as the sputtering power is increased for a fixed sputtering pressure, the deposition rate increases linearly. The sputtering rates for the materials grown in this study are listed in Table 2.1. These rates were based on relatively new target surface. As targets continue to sputter, a wear track forms and the rate will decrease. Careful calibration for sputtering rates should be frequently conducted to ensure a proper growth thickness of the individual layers. The thickness of the individual layers, determined by the rate of sputtering, is reflective of the phase of the deposited film. Even though the flux of atoms that are ejected from the target surface is the same, the stacking sequence of the deposited atoms, which is used to determine the rate (film thickness per time of deposition) can vary. For example, the inter-atomic stacking sequence for the bulk equilibrium phase may not
Fig. 2.2 Linear increase in sputtering rate for $bcc$ Nb with an increase in sputtering power at 2-4 mTorr Ar.

Table 2.1 Rate of Phase Deposition

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>bcc Nb</th>
<th>hcp Nb</th>
<th>hcp Zr</th>
<th>bcc Zr</th>
<th>hcp Ti</th>
<th>bcc Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.022</td>
<td>0.040</td>
<td>0.032</td>
<td>0.026</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>100</td>
<td>0.090</td>
<td>0.150</td>
<td>0.115</td>
<td>0.116</td>
<td>0.049</td>
<td>0.076</td>
</tr>
<tr>
<td>200</td>
<td>0.219</td>
<td>----</td>
<td>0.275</td>
<td>0.334</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>
necessarily be the same for the pseudomorphic phase. Even though these differences are typically tenths of an angstrom, phase transformations are on the order of 4-10 monolayers. Thus, small inter-atomic differences at this length scale can have a dramatic effect on the rate used in the growth of the individual layers for a specific bilayer thickness. In determining the multilayer’s phases to be grown, appropriate rates should be extended. Obviously as the film grows in thickness and transforms to a bulk equilibrium structure, the pseudomorphic rate is no longer applicable; these rates, are phase (thickness) dependent. The sputtering rates were determined by the volume fractions of each material in the multilayer stack coupled to the bilayer spacing determined by reflection X-ray diffraction (see Section 2.2).

2.1.2 Magnetron Sputtering

The formation of the glow discharge used in sputtering occurs by the ionization of the working sputtering gas. As a negative potential is applied to the surface of the target, the working gas’s electrons and positive nucleus are polarized and eventually ionized in a low-pressure environment [3]. This ionized state of free electrons and ions is termed a plasma because of the unique fluidity properties associated with these charged particles.

In the initial stages of a dc glow, a small amount of initial charge carriers are introduced into the system. As the voltage potential increases, the charge carriers acquire more energy and produce more charge carriers by ion collisions with the cathode (target) [1]. These collisions result in the release of secondary ions that ionize more of the neutral working gas atoms. During this period the current will increase but the voltage will remain
the same because of the high impedance of the power supply connected to the cathode (target) surface. In this process large amounts of electrons and ions are produced. Once the electrons generate enough ions which can regenerate the initial number of electrons, a self-sustaining plasma is achieved and the gas glows.

To achieve effective sputtering, a Lorentz force is used to influence the pathways of the plasma’s charged species. The Lorentz force is given as [2]

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$  \hspace{1cm} (2.2)

where $q$ is the charge, $\mathbf{E}$ is the electric field vector, $\mathbf{v}$ is the velocity vector, and $\mathbf{B}$ is the magnetic field vector. Since the electrons have a much smaller mass than the ions within the plasma, they are much more mobile and respond quicker to the influence of the Lorentz force. This will be critical in defining a plasma region above the target surface for sputtering.

When the negative electric field is applied to the target, the positive ions are accelerated towards the target surface as the electrons move in the opposite direction. If a permanent magnet is placed under the target surface with a closed field loop, as shown in Fig. 2.3, the electrons can become trapped by the Lorentz force [1]. Initially the electrons are parallel or nearly parallel to the magnetic field lines as they accelerate from the negatively charge surface. Eventually the magnetic field lines bend over, termed the magnetron component, and run parallel to the surface. The electrons, at the magnetron component position, experience the $\mathbf{v} \times \mathbf{B}$ term of Eq. (2.2) and are forced back towards the negatively charged surface. Once the electrons approach the target surface, the Coulombic interaction will again force the electrons away and the cycle repeats. The electrons are now trapped between an electric field force and a magnetron field force. They move in a helical path as
Fig. 2.3 A representation of the working principles of magnetron sputtering [1].
they travel between the upper and lower limits governed by the electric and magnetic fields. The trapped electrons continually ionize the gas in a specific region above the target. Since the plasma is confined to a specific region above the target surface in which positive ions are extracted and used to sputter the surface, an erosion track will form on the surface.

2.1.3 Deposition Chamber

The magnetron sputtered Zr/Nb and Ti/Nb multilayered films were grown on either {111} Si wafers that had a 200 nm thick amorphous oxide surface layer or {001} Si wafers with a native oxide surface. In each case, the oxide surface and ambient deposition temperature prevented any epitaxial orientation relationship to develop between the deposited film and substrate surface. The films were grown over a 2-inch diameter wafer. The 3-inch diameter sputtering targets ensured a uniform thickness over the entire deposited surface of the wafer. The wafer was rotated, automatically by a LabVIEW® program, between the two sputtering sources (Zr or Ti and Nb) to deposit the alternating A/B multilayered structure for 40-60 layer pairs. Sputtering power were regulated at 25 W, 100 W, and 200 W depending upon the control rate needed in growing the multilayers. Ultra-high-purity Ar was used as the working gas at a pressure of 2-4 mTorr. The stainless steel sputtering chamber has an optimal base pressure of ~ 4 x 10^{-9} Torr. Residual gas analysis has shown that the background gases of hydrogen, nitrogen, and oxygen are below scale (10^{-9} Torr) and that water vapor comprises the background base pressure. The chamber can be baked out to 200°C using an internal halogen lamp set at 120 V AC. Substrates are lowered and retrieved in the chamber.
Fig. 2.4 The UHV sputtering deposition chamber
by a load lock. Fig. 2.4 is a picture of the sputtering chamber with corresponding equipment labeled.

2.2 X-ray Diffraction

X-ray diffraction (XRD) provides a characterization technique that requires no sample preparation and is nondestructive. This is particularly useful in preventing sample preparation artifacts that could stabilize the pseudomorphic phases. Two different diffraction orientations have been used in the characterization of the multilayered thin films, reflection XRD and transmission XRD. Since the films are polycrystalline but exhibit a preferred growth texture as discussed in Chapter 1’s Section 1.2, specific diffraction orientations can be more useful in phase identification.

2.2.1 Reflection X-ray Diffraction

Reflection XRD (RXRD) was performed in the Bragg-Brentano geometry. Since thin films will grow from a substrate surface that minimizes their surface energy, thin films and multilayers exhibit a preferred growth texture [4]. Even if the film grows polycrystalline on the surface of the substrate, each grain will share the same common out-of-plane texture. Typically this is the closest packed planes for that phase. In the Bragg-Brentano geometry, only the preferred growth texture will meet the diffraction condition of Bragg’s law [5]

\[ n\lambda = 2dsin\theta \]  

(2.3)
where \( n \) is the order of the diffracted peak, \( \lambda \) is the x-ray radiation wavelength, \( d \) is the diffracting lattice spacing of the planes, and \( \theta \) is the diffracted angle. Unfortunately the film’s texture limits the phase identification to one or a few peaks. Phase identification can be very difficult in this diffraction orientation due to the low number of identifying peaks. For example, if two phases share nearly an identical d-spacing for the textured planes, it is difficult to determine if one of the phases has undergone a change in phase stability due to the overlapping of the diffracted out-of-plane intensities. If the peak shifts, that does not necessarily indicate a change in phase but could be a response to elastic strains at the interface. Finally, as multilayered thin films reduced in thickness, individual \{hkl\} diffracting peaks can average into a single peak [6]. This is due to the low number of available atoms in the diffraction volume in this orientation. An example of this is illustrated in Fig. 2.5 for Cu/Nb multilayers [6]. A detailed derivation of the diffracted intensity as a function of layer spacing and number of diffraction atoms can be found in the work of Segmuller and Blakeslee [7] and Schuller [8].

Even with these complications, the RXRD geometry can provide valuable information concerning the multilayer structure. Besides being able to identify out-of-plane texture, the chemical modulation (bilayer spacing) of the multilayer can be found. Centered about the primary \{hkl\} textured reflection, satellite reflections on either side of the primary peak, can develop depending on the alignment of the goniometer and quality of the chemical modulation of the multilayer. The mathematical diffraction details for the formation of satellite peaks can be referenced elsewhere [6]. The separation of these peaks are given as

\[
 n\lambda = 2\Lambda \sin(\Delta\theta)
\]  

(2.4)
Fig. 2.5 Averaging of the diffracted \{hkl\} intensities of a Cu/Nb multilayer from the individual Cu and Nb layers as the bilayer thickness is reduced. Such diffraction events in RXRD can make phase identification of pseudomorphic phases difficult [6].
where \( n \) is the order of the satellite reflection, \( \lambda \) is the radiation wavelength, \( \Lambda \) is the bilayer spacing, and \( \Delta \theta \) is the diffraction angle difference between the satellite intensity peak and the primary \( \{hk\ell\} \) textured peak. Eq. (2.4) was used to determined the average bilayer spacing of the multilayers grown in this research. Recall from Chapter 1, the biphase stability diagram requires the bilayer spacing of the multilayer in determining the biphase stability boundaries.

RXRD was performed on a Scintag XDS 2000 diffractometer. The scan rates were continuous at 0.5°/min. with a chopper increment of 0.03°. The source utilized 2 mm and 4 mm slits while the detector was equipped with 0.5 mm and 0.3 mm slits. CuK\(_\alpha\) radiation (1.54 Å) was used as the source radiation.

### 2.2.2 Transmission X-ray Diffraction

Unlike RXRD where only the textured growth planes of the individual phases meet the diffraction condition, in-plane or transmission XRD (TXRD) of the polycrystalline film allows for multiple \( \{hk\ell\} \) diffraction events due to the polycrystalline growth in-plane. The additional \( \{hk\ell\} \) intensities allow for conclusive evidence of phase transformations within the film. TXRD was performed at Argonne National Laboratory’s Advanced Photon Source (APS). The APS facility utilized was the University-National Laboratory-Industrial Collaborative Access Team (UNI-CAT) Beam-Line 33-BM (bending magnet). Figs. 2.6 (a)-(d) are images of the experimental set-up. The APS energy was fixed at 15.05 keV (0.822 Å). At this energy, the radiation was sufficient to penetrate through the approximately
400 nm thick multilayer film and the 350 µm thick silicon substrate with a beam intensity loss of 70%. This type of experimental set-up allows for the multilayers to be characterized on the substrate in the as-deposited condition.

The diffracted intensities were collected in a step scan at increments of 0.03° for a collection of 400K counts/step. The incident slit and detector slit were set at 0.5 mm x 0.5 mm and 18 mm x 0.5 mm respectively. The Si substrate, being a single crystal, allowed its Bragg diffracted intensities to be tilted away from the angle of detection of the detector. Though thermal diffuse scattering bands [9] from the Si wafer can raise the background intensity level. Fig. 2.7(a) is a Lowe TRXD image that shows the overlap of a thermal diffuse scattering band and a multilayer’s diffracted ring intensities. Fig. 2.7(b) is the corresponding plot of the intensity verses 2θ angle of diffraction. Comparison of Fig. 2.7(b) to Fig. 2.7(a) clearly indicates that the thermal diffuse scattering raises the background intensity. As shown by Holt et al. [9], the thermal diffuse scattering bands are symmetric with crystal symmetry of the Si wafer and were rotated on the goniometer such that the thermal diffuse band did not overlap the ring intensity of the multilayer. To further reduce the thermal diffuse scattering, some of the specimens were mechanically ground with SiC from the Si side to 100 µm in thickness and then dimpled ground to 30 µm to reduce the scattering volume contribution of the Si wafer.
Fig. 2.6 (a) Transmission XRD experimental set-up at the APS (b) Tubing from the detector to the specimen was used to reduce x-ray scattering from the air (c) Tripod surveyor was used to align the specimen to the focusing circle of the goniometer (d) Goniometer
Fig. 2.7 (a) A transmission XRD Lowe image of a bcc Ti / bcc Nb multilayer. The ring intensity of the film is overlapped by the presence of thermal diffuse scattering (TDS) bands from the Si substrate (b) The corresponding intensity scan verses 2θ. Comparison to (a) clearly indicates that the TDS raises the background level intensity.
2.3 Volume Fraction Determination

The separation in the satellite peaks in the RXRD experiments were used to determine the bilayer spacing, $\lambda$, of the multilayers for the biphase diagram. To determine the volume fraction of the constituent phases, Energy Dispersive Spectroscopy (EDS) was performed on the multilayers in a FEI/Philips XL 30 Field Emission Gun (FEG) Scanning Electron Microscope (SEM). A spot size of 3 with an accelerating voltage of 15 keV were the SEM operating parameters. Counts per second ranged from 1200-2000 with 20%-30% dead time. EDS ZAF software was used to quantify the atomic percentage of each material in the multilayer stack. The Zr and Ti K$_{\alpha}$ and the Nb L energies were used in determining the atomic percentage of each element in the multilayer. Coupling the atomic percentage of EDS with the bilayer spacing, $\lambda$, and the density (phase of the material) of the constituent layer within the multilayer, the volume fraction was determined by the following series of equations:

$$ EDS_A = \frac{[\rho_A \cdot V_A]}{[\rho_A \cdot V_A + \rho_B \cdot V_B]} \quad (2.5) $$

$$ \lambda = h_A + h_B \quad (2.6) $$

$$ V_i = A \cdot h_i \quad (2.7) $$

where $EDS_A$ is the atomic percentage of $A$ from EDS, $\rho_i$ is the density of $i$, $V_i$ is the volume of $i$, $\lambda$ is the bilayer spacing, and $A$ is the surface area of the film which is a constant. Eq. (2.5) can be reduced by substitution of Eq. (2.6) and Eq. (2.7) to give

$$ h_A = -\frac{[\lambda \cdot \rho_B \cdot EDS_A]}{[\{EDS_A \cdot (\rho_A - \rho_B)\} - \rho_A]} \quad (2.8) $$

The volume fraction of $A$, $f_A$, is then

$$ f_A = \frac{(A \cdot h_A)}{A \cdot (h_A + h_B)} = \frac{h_A}{\lambda} \quad (2.9) $$
2.4 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was used to determine the microstructure and phase of the deposited multilayers. In Section 2.4.3, a detailed description of TEM specimen dependent artifacts will be discussed. There has been considerable confusion in the validity of phase identification of pseudomorphic phase stability by TEM diffraction. The multilayers reported in this work have been prepared in both the cross-section and plan-view orientations. The cross-section and plan-view foils are in the same diffraction condition as RXRD and TXRD respectively. Microscopy of the foils were performed in a Philips CM 200 TEM operating at 200 KeV.

2.4.1 Cross-section TEM

Cross-section TEM was used to determine the microstructure of the multilayered stack. The cross-section foils were prepared by two different techniques: Conventional ion milling and Focus Ion Beam (FIB) milling [37].

The conventional ion milling samples were prepared by diamond tip scribing and subsequent cleaving of the Si wafer substrate, with the deposited film, into two 2.9 mm x 1.0 mm rectangular sections. These rectangular sections were then glued to each other with film-facing-film using a M-Bond epoxy. The epoxy needs to be carefully brushed across the surface of the film to ensure uniform coverage. After being glued, the two-rectangular specimens were slowly cured from room temperature to 60°C for 24 hours. While raising
the curing temperature, it should be done slowly to prevent air bubbles forming at the interface in the epoxy. Once cured, the rectangular specimen was sectioned into 1-2 mm smaller pieces using a diamond saw. These sub-rectangular sections were then glued to a 3 mm diameter 300 μm thick copper ring. The specimen with ring was then mechanically ground to 100 μm in thickness using SiC 600 grit paper. The specimen was then finally dimple ground with a 15 μm diamond paste and oil mixture using a Gatan Dimpler grind wheel centered at the film-facing-film interface. The dimpled divot formed at the interface was 15 μm in thickness. The specimen was then Ar ion milled at 9°-10° to electron transparency at a setting of 5.5 keV 0.5 mA.

Using a FEI Dual Beam-235 Focus Ion Beam instrument, cross-section TEM foils can be made much more rapidly then conventional ion milling techniques [31]. The specimens were directly placed onto a SEM stub and loaded into the DB-235 chamber. After proper alignment of the specimen to the e-beam, it was tilted such that the surface of the film is normal to the Ga ion milling source. As shown in Fig. 2.8(a), a protective Pt surface layer is deposited onto the desired specimen location. The Pt serves as a buffer layer from ion implantation of the Ga ions into the specimen. Automated software was then used to mill two trenches on either side of the desired foil location. Iterative milling eventually brings the trenches closer together until a 100 nm thick (electron transparent) slice remains as seen in Fig. 2.8(b). This foil is then ion milled at the two edges to free it from the trench as shown in figure 2.8(c). The foil can then be lifted out of the trench and placed onto a carbon coated TEM grid using a micro-manipulator.
Fig. 2.8 (a) In-situ SEM image of a cross-section TEM foil being prepared by FIB milling. Pt cap is deposited onto the surface to be a sacrificial protective cover of the multilayer beneath it. (b) Ga+ ion image of the cross-section foil. The foil needs to be milled to a thickness of \( \approx 100 \) nm for electron transparency (c) Once the foil has been milled, the side walls are cut and the foil is ready for retrieval.
2.4.2 Plan-view TEM

Plan-view electron diffraction provides the most useful orientation for phase identification. As stated in the XRD section, the films exhibit a preferred growth texture out-of-plane but a random in-plane polycrystalline morphology. The plan-view specimens are able to diffract multiple \{hkl\} intensities in this orientation. Even though the grains are random to each other, the layering of the A/B films within the grain can exhibit a preferred orientation relationship between each of the A/B layers. The in-plane orientation relationship of the A/B phases can be determined by the textured intensities within the in-plane diffracted rings. The alignment or angular displacement of one phase’s \{hkl\} ring's textured intensity to that of another phase’s \{hkl\} ring’s textured intensity was used to determine the orientation relationship. This was also confirmed by Convergent Beam Electron Diffraction (CBED) patterns from the individual grains. By reducing the C2 aperture and beam’s spot size, the CBED diffracted intensity spots’ diameters are reduced and can be used for accurate indexing of the orientation relationship. The preferred out-of-plane growth texture combined with the in-plane parallel directions were used to determine the A/B orientation relationship. The d-spacing value associated with the \{hkl\} ring was calculated by measuring the projected radius of the ring and applying it to the following equation [10]:

\[
dR = \frac{\lambda}{L}
\]

where \(d\) is the lattice spacing for the diffracted \{hkl\} plane, \(R\) is the measured radial projection of the ring, \(\lambda\) is the radiation wavelength, and \(L\) is the camera length. The camera length was determined by using an Al standard diffraction pattern.
The plan-view TEM foils were prepared by convention ion milling. The Si wafer, with the deposited multilayer, was ultrasonically drilled using a SiC slurry into 3 mm diameter discs. Using 600 grit SiC paper, these disc were ground from the Si side, while protecting the film side, to 100 µm in thickness. The discs were then dimpled ground to 15 µm in thickness at the center of the disc and subsequently Ar ion milled from the Si side at 9°-10° until electron transparency. The ion mill was set at 5.5 keV 0.5 mA with the disc rotating at 10 rpm.

2.4.3 Resolving the Issue of TEM Specimen Preparation Artifacts

In recent years, considerable debate has been generated on proper phase stability identification using electron beam diffraction. It is been shown that TEM foil preparation may artificially stabilize pseudomorphic phases. For example, Huja et al. [11] and Banerjee et al. [12] reported the stabilization of fcc Ti in Ti/Al multilayers through cross-section TEM diffraction. Previously and subsequently to these reports, others have observed fcc Ti in Ti/Al [13-19], Ti/Ag [20], Ti/Ni [21], and in Ti/Zr [22] multilayers. Tepper et al. [20] originally speculated that a reduction in surface free energy may compensate for the bulk free energy increase for a Ti transformation in Ti/Ag multilayers. As discussed in Chapter 1, Dregia et al. [23] have constructed a model based on classical thermodynamics to predict phase stability as a function of these thermodynamic properties. Subsequently to the first report by Tepper et al. [20], Tepper et al. [22] concluded that the transformations are due to hydrogen stabilized fcc Ti during TEM sample preparation for electron diffraction studies.
Hydrogen primarily from the hydrocarbon-based vacuum pumping oils used in the vacuum ion milling step of TEM foil preparation is believed to be the source of the contamination. van Heerden et al. [13], Josell et al.[19], and Bonevich et al. [16-17] have also contributed $\text{fcc} \text{Ti}$ in Ti/$\text{fcc}$ metal multilayers to being an artifact of sample preparation. In each of their studies, TEM cross-section electron diffraction, Bragg XRD, and transmission XRD were used. In the cross-section electron diffraction, the $\text{fcc} \text{Ti}$ was observed but subsequently not observed in the x-ray diffraction. Banerjee et al. [14-15] have also noted $\text{hcp}$ and $\text{fcc}$ discrepancies in Ti for electron diffraction between the cross-section and plan-view geometry. They have concluded that the plan-view diffraction results are not artifacts of hydrogen stabilized $\text{fcc}$ but rather $\text{fcc} \text{Ti}$ stabilized by the interfacial energy. Banerjee et al. [15] have been able to indicate how hydrogen can act as an alloying agent to alter the transformation thickness to stabilize the $\text{fcc}$ phase and that an interfacial energy stabilization thickness is still possible for $\text{fcc} \text{Ti}$. Contrary to this report, van Heerden et al. [13] have calculated the theoretical energy barrier necessary for $\text{hcp}$ to $\text{fcc}$ Ti transformation and has suggested that it is to high to be stabilized by interfacial free energy. Tepper et al. [22] has shown $\text{fcc}$ stabilization for both Zr and Ti in a Zr/Ti multilayer in the cross-section and plan-view geometry. Bonevich et al. [16] have reported $\text{fcc}$ Ti due to hydrogen in plan-view TEM diffraction. Even though this work is to investigate $\text{hcp}$ to $\text{bcc}$ phase stability for Ti and Zr, the use of electron diffraction as a legitimate phase identification technique needs to be clearly established as evident by the current confusion in the literature over artifacts in pseudomorphic phase stability.
The inconsistency of phase identification between the plan-view and cross-section TEM foils for the Ti/fcc multilayers can be understood in terms of the multilayer’s orientation to the Ar⁺ milling source during electron transparency thinning. In plan-view milling, the outer most layer can be a diffusion barrier cap to hydrogen interdiffusion into the multilayer stack as illustrated in Fig. 2.9(a). For Ti/Al multilayers, the diffusivity of hydrogen in Al is much less than that of Ti [24]. Even if the outer most layer of the multilayer is Ti, that Ti surface layer will be fcc hydrogen stabilized, and the Al layer underneath this surface layer can prevent further diffusion of hydrogen into the multilayer stack. As shown in Fig. 2.9(b), in the cross-section geometry, the entire stack of freshly milled layers is exposed to the atmospheric surface. In this orientation, the Al layer can not act as a diffusion barrier to hydrogen, thus all the Ti layers are exposed to hydrogen contamination and a hydrogen stabilized fcc phase can result. This simple diffusion cap model explains the discrepancies between the plan-view and cross-section diffraction patterns observed by van Heerden et al. [13], Josell et al. [19], Banerjee et al. [14-15], and Tepper et al. [20]. van Heerden et al. [13] have commented that milling geometry is inconsistent with contamination, but in their own report they note a discrepancy between hcp Ti in the plan-view and fcc Ti in the cross-section for Ti/Al multilayers. Their cross-section fcc Ti has a lattice parameter of 4.40 Å, consistent with the fcc δ-TiH₂ phase. They are unable to rationalize this discrepancy with any of their proposed models.

Tepper et al. [22] had hydrogen stabilized fcc phases for both the plan-view and cross-section electron diffraction geometry for a Zr/Ti multilayer. This result is also consistent with the proposed diffusion cap layer model. Unlike the Al based multilayers, each individual
Fig. 2.9 Representation of a diffusion-cap model to explain the hydrogen stabilized $fcc$ $\delta$-TiH$_2$ phases in Ti/$fcc$ multilayers. (a) Plan-view milling geometry. The outer layer can act as a diffusion barrier cap for the infiltration of hydrogen into the multilayer stack (b) Cross-section milling geometry. In this orientation all of the freshly milled interfaces are exposed to atmosphere and hydrogen can contaminate the entire stack generating a sample preparation artifact.
layer in the $hcp\ Zr/\ hcp\ Ti$ multilayer has a high affinity for hydrogen [24]. During the plan-view ion milling process neither Zr nor Ti will act as a diffusion barrier for the absorption of hydrogen into the entire multilayer stack. This allows the multilayer in either orientation to convert to a hydrogen-stabilized structure for both materials. Without this diffusion barrier cap, hydrogen contamination would be suspected for either plan-view or cross-section orientations.

Bonevich et al. [16] have reported fcc Ti, stabilized by hydrogen, in both the cross-section and plan-view TEM geometry for a Ti/Al multilayer. This result would seem to contradict the proposed diffusion cap model. As an be seen in the plan-view diffraction pattern in Fig. 2.10(a), Bonevich et al.’s [16] indexed a series of \{111\} and \{311\} reflections for fcc Ti, with a lattice value $4.35\ \text{Å}$, in a [111] zone axis. Since these are forbidden reflections in this diffraction orientation, they rationalized their observation as rel-rods of fcc Ti in the pattern. The \{111\} type reflections have a similar d-spacing as the $hcp\ Ti$’s \{1010\} reflections, i.e. $2.511\ \text{Å}$ and $2.552\ \text{Å}$ respectively. Both of these reflections would exhibit the same type of crystallographic symmetry and orientation relationship to the fcc Al plane as shown in the simulated diffraction patterns of Fig. 2.10(b) and Fig. 2.10(c). The \{1010\} reflection is not a forbidden reflection in this zone axis and would be the expected to diffract for bulk $hcp\ Ti$. Using the \{220\} Al reflection with a d-spacing $1.43\ \text{Å}$ and whose position is the greater radial \{220\} split intensity spot in Bonevich et al.’s [16] plan-view diffraction pattern of Fig. 2.10(a), the calculated camera constant was found to be $93.67\ \text{mm-Å}$. In either the $hcp\ Ti$ or fcc Ti interpretation of the diffraction pattern of Fig. 2.10(a), the \{220\} Al d-spacing is smaller then \{220\} fcc Ti ($1.54\ \text{Å}$) or \{1120\} $hcp\ Ti$. 

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**Fig. 2.10** (a) The plan-view diffraction pattern of a Ti/Al multilayer taken from Bonevich *et al.* [16] article (figure 4(a) in [16]) (b) Simulated plan-view electron diffraction pattern for a *fcc* δ-TiH$_2$/*fcc* Al multilayer (c) Simulated plan-view electron diffracted pattern for a *hcp* Ti/*fcc* Al multilayer.
(1.48 Å) spots. Therefore, the \{220\} Al spot is in the same position for the split in either reference frame for calculating the camera constant. Using this value, the \{111\} d-spacing reflection was measured to be \(\sim 2.5\) Å which matches well to the d-spacings of \{111\} \(fcc\) \(\delta\)-TiH\(_2\) or \{10\(\bar{1}\)0\} \(hcp\) Ti. But the \{111\} rel-rod reflection, not being an allowed reflection in this zone-axis, would have a projection of itself onto this plane with a d-spacing of 2.37 Å. The measurable discrepancy of the projected \{111\} reflection’s d-spacing to the measured d-spacing strongly suggests that this film, in the plan-view orientation, is \(hcp\). Similarly, the \{311\} \(fcc\) TiH\(_2\) reflection has a d-spacing of 1.31 Å but a projection of 1.29 Å on the (111) plane. As seen in the simulation of Fig. 2.10(c), this reflection has same crystallographic orientation position and similar d-spacing value for \(hcp\) Ti \{20\(\bar{2}\)0\}. Again, this bulk \(hcp\) reflection, with a d-spacing of 1.28 Å, is an allowed reflection in this zone axis. The measured d-spacing of Fig. 2.10(a) was 1.28 Å. The \{220\} split reflections in the pattern of Fig. 2.10(a) was contributed to the \(fcc\) TiH\(_2\) and \(fcc\) Al phases. From the simulations of Figs. 2.10(b) and (c), the \(fcc\) TiH\(_2\) \{220\} reflection has the same crystallographic orientation position as \(hcp\) Ti’s \{11\(\bar{2}\)0\} reflection and a similar d-spacing, i.e. 1.48 Å for the \(hcp\) Ti phase and 1.53 Å for the \(fcc\) \(\delta\)-TiH\(_2\) phase. We have measured the d-spacing to be 1.51 Å. van Heerden \textit{et al.} [13], similar to the reported work of Banerjee \textit{et al.} [15], observed \(hcp\) Ti in the plan-view and \(fcc\) \(\delta\)-TiH\(_2\) in the cross-section geometry for all of their Ti/Al multilayers. It is concluded that the proposed plan-view \(fcc\) Ti pattern in the Ti/Al multilayer reported by Bonevich \textit{et al.} [16] was mis-indexed and is \(hcp\) Ti. This result would make it consistent the diffusion cap model and other reports in the literature.
2.4.3.1 Resolving the Issue of $f_{cc}$ Ti

Finally, Bonevich et al. [16] provided, at its time, a comprehensive investigation of two Ti/Al multilayers with a bilayer spacing of 7.2 nm and 5.2 nm with approximately equal volume fractions ($f_{Ti} \approx 50\%$). These length scales were based upon the initial $f_{cc}$ Ti results of Huja et al. [11] and Banerjee et al. [12]. Subsequently Banerjee et al. [18] have indicated that hydrogen contamination had altered the $f_{cc}$ indexed cross-section results. In Bonevich et al.’s [16] results, only the $f_{cc}$ phase was present in the cross-section diffraction pattern (and not in the transmission XRD results) leading to a conclusion that the $f_{cc}$ Ti in Ti/Al multilayers were artifacts.

Subsequently, Banerjee et al. [15] has been able to index, in the plan-view electron diffraction geometry, a coherent $f_{cc}$ Ti / $f_{cc}$ Al multilayer with a bilayer spacing of 8.1 nm. The lattice parameter for these $f_{cc}$ phases is 4.05 Å. This is in good agreement with the theoretical predictions of $f_{cc}$ Ti by Paxton et al. [25]. The $f_{cc}$ $\delta$-TiH$_2$ lattice value is $\approx$ 4.40 Å. As discussed in Chapter 1, the classical thermodynamic treatment of phase stability in multilayers requires volume fraction as well as bilayer thickness in determining the phase stability [23]. Even though Banerjee et al.’s [15] bilayer spacing is larger then Bonevich et al.’s [16] Ti/Al multilayers, Banerjee et al.’s [15] film only had a volume fraction of 18 % Ti, much less then Bonevich et al.’s [16] 50 % Ti. By reducing the volume fraction of Ti, even though the bilayer was larger, it was possible to stabilize $f_{cc}$ Ti. As correctly pointed out by van Heerden et al. [13], Dregia et al. [23] and Tepper et al.[20], a reduction in interfacial energy could help stabilize a $f_{cc}$ Ti phase.
van Heerden et al. [12] have suggested that the interfacial free energy necessary to stabilize fcc Ti in Ti/Al multilayers is too large and could not be a stabilizing factor. The calculation that van Heerden et al. [13] used to assess this interfacial free energy necessary to stabilize fcc Ti was based upon a 750 nm Ti / 45 nm Al multilayer. This multilayer was shown to be hcp Ti in the plan-view diffraction geometry and fcc Ti in the cross-section geometry with a lattice value of fcc δ-TiH₂ [13]. As explained above, this transformation is an artifact of fcc stabilized TiH₂ and not interfacial energy. The plan-view diffraction pattern clearly indicated the hcp Ti phase. Even with this discrepancy, van Heerden et al. [13] used this multilayer to calculate the interfacial free energy for stabilizing the fcc Ti phase. Based upon the assumption that the atomic volumes of hcp and fcc Ti are approximately equal, the interfacial energy difference necessary to stabilize fcc Ti by van Heerden was given as

$$\Delta[\gamma] < -N_{Ti}\Delta[\mu]/2\Omega_{Ti}^{2/3}$$

(2.11)

where $\Delta[\gamma]$ is the interfacial free energy difference, $N_{Ti}$ is the number of Ti atomic planes in one Ti layer from the Ti/Al interface, $\Delta[\mu]$ is the activation energy barrier for hcp Ti to fcc Ti transformation and was taken to equal 0.08 eV/atom (= 1.3x10⁻³⁰J/atom) [25], and $\Omega_{Ti}$ is the atomic volume of Ti. The 750 nm Ti / 45 nm Al multilayer would require a $\Delta[\gamma] < -311$ J/m². Correctly pointed out by the authors [13], this value is unrealistic. The authors [10] then concluded that the $\Delta[\mu]$ value by Paxton et al. [25] is inappropriate for this calculation. Using the volume fraction (number of atomic planes, $N_{Ti}$) of Ti for the fcc Ti stabilized phase by Banerjee et al.[15], the $\Delta[\gamma]$ was calculated to be approximately 670 mJ/m², a value typical of solid-solid interfacial energies [26]. The large volume fraction of Ti in van Heerden et al.’s [13] calculation generated the erroneous value and not the atomic bonding
potential energy given by Paxton et al. [25]. The $\Delta[\mu]$ of Eq. (2.11) can generate realistic interfacial energy values when an appropriate volume fraction for a stabilized fcc Ti, not by hydrogen, is used in the calculation.

Bonevich et al.’s [16-17] general conclusion that fcc Ti is an artifact in Ti/Al multilayers is incorrect. Their results [16-17] and others [13,19] were based upon a much larger volume fraction of Ti. It is premature to discount the possibility of interfacial energy stabilized fcc Ti in other Ti/fcc metal multilayers. In such systems the appropriate combination of volume fraction and bilayer thickness may not have been deposited. It is now possible to reconcile the differences observed by various research groups if volume fraction as well as electron diffraction geometry (plan-view verses cross-section) are carefully reported.

In conclusion, plan-view electron diffraction can be a legitimate technique in properly identifying phase stability without artifacts in multilayered thin films. Special attention must be used for correctly indexing diffraction patterns in the cross-section where specimen artifacts can occur more readily. Nb, like Al, has a low solubility for $H_2$ at room temperature [24] and should act as a diffusion barrier cap for the Zr/Nb and Ti/Nb multilayers grown in this study. If fcc hydrides form, they will be readily observable since the phase stability of the Zr and Ti should be bcc.

2.5 3D Atom Probe Tomography

In each of the models proposed to explain phase stability in multilayered thin films, the chemical profile at the interface for the A/B multilayers is critical. Asta et al. [27] have
shown that 5% intermixing at the interface between Al and Ti would result in the $\Delta G_{\text{Al}}$ exceeding the value of $\Delta G_{\text{Ti}}$ for Ti/Al multilayers. It is therefore critical to establish the chemical composition and possible interdiffusion that would exist at the interface of the multilayer. Nb, which is a $\beta$-stabilizer for both Zr and Ti, could have a significant role in helping to facilitate $bcc$ phase stability in the Zr and Ti layers.

3D Atom Probe Tomography is a technique that is ideally suited to yield such information due to its high spatial resolution [28]. The atom probe technique works by pulsating a dc voltage onto a very fine tip specimen that has a radius of curvature of $\approx 50$ nm. The small radius of curvature allows for the electric field at the tip to be very large (3-4 V/nm). The field, $F$, at the apex is [28]

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

(2.12)

where $V$ is the applied voltage, $r$ is the tip radius, and $k$ is a numeric constant. The application of the strong electric field causes the atoms at the apex to field evaporate. As the tip’s radius continues to increase in size with the evaporation of atoms off the apex, larger voltages are required for field evaporation. In the work conducted, field evaporation typically started near 5 kV and continued up to 15 kV as the radius of curvature decreased as the tip field evaporated. The specimen was allowed 20 minutes to accommodate to a temperature of 50 K prior to field evaporation. Field evaporation was conducted at a pulse fraction of 20% above the base voltage with a pulse repetition of 1.5kHz. Prior to field evaporating the tip for atom probe collection, a field ion image of the tip was taken. Fig. 2.11 is an image of the atom probe instrumentation.
Field ion imaging of the tip occurs by flowing in an image gas, Xeon for this study, into the chamber to a pressure of $5 \times 10^{-5}$ mBar and applying an electric potential to the tip. The image gas atoms are polarized near the tip once an appropriate voltage is reached. This is typically 4-6 kV depending upon the curvature of the apex. The tip, being cryogenically cooled, can thermally accommodate the polarized image gas atoms on the atomic terraces of the specimen’s tip [28]. As the applied voltage is increased, the image gas on the surface is field ionized by an electron tunneling process. The image gas ions are then repelled from the surface and collected on a phosphorus screen. The distribution of light intensity spots on the screen represents the atomic location of the individual atoms on the surface of the tip. A field ion image of a Ti/Nb tip is shown in Fig. 2.12.

Once a suitable tip is imaged to ensure a sufficient radius of curvature, the imaging gas is evacuated out of the chamber and the tip is field evaporated for the collection of atoms. The field evaporation function, $Q_n$, for an n-fold charged ion under a zero field condition is given as [28]

$$Q_n = \Lambda + \Sigma I_n - n\phi$$  \hspace{1cm} (2.13)

where $\Lambda$ is the heat of sublimation, $I_n$ is the n\textsuperscript{th} ionization energy, and $\phi$ is the work function from the emitting surface. Normally ionic states are metastable as compared to neutral states, but under an applied electric field, the ionic states of the surface atoms are more stable at a distance from the potential surface. At a particular distance from the surface, the ionic and neutral potential energy curves intersect and the removal of an ion becomes possible [39]. As shown in Fig. 2.13, once an ion is field evaporated off the tip, it is passed through an energy filtering field and deflected to a negatively charged detector. The time of flight
Fig. 2.11 Atom probe experimental equipment [28].

Fig. 2.12 Field ion micrograph image of the Ti/Nb multilayer tip at 12.9 kV 60 K.
Fig. 2.13 (a) Illustration of atom probe field evaporation of a specimen tip with subsequent capture of the atoms spatial position on a x-y detector [28] (b) For improved chemical analysis of the ions, they are passed through in energy filter prior to collection [28].
and position it strikes the detector can be used to reconstruct its location from the tip’s surface [28]. The mass-to-charge ratio of the ion is then used to identify the type of atom. Combining the position to the type of atom allows for a 3D reconstruction of the specimen. Occasionally, as the electric field is applied during the field evaporation procedure, the tip will break due to a defect in the tip that is exposed to the high stress from the electric field force. This is commonly referred to as a ‘flash.’ After a flash, the tip’s radius is typically too large to continue to field evaporate.

2.5.1 Atom Probe Specimen Preparation

To collect an atom probe chemical profile of the layered interfaces, the multilayer stack needs to be normal to the apex of the tip as shown in the TEM bright-field image of Fig. 2.14. A 5 Ω−cm n-doped (001) Si wafer was used as the substrate for the atom probe multilayers. Obviously, the tip, and all subsequent materials leading to the tip, must be conductive in order to apply the necessary electric potential required for field evaporation. To form the atom probe tip, a multi-process preparation procedure, similar to Martens et al. [29], was utilized.

A 5 µm x 5 µm island pattern, using standard photolithography techniques was layered onto the surface of the Si wafer substrates at Cornell University’s Nanofabrication Facility. Once the photolithography steps were completed, the wafers were ‘Bosch-etched.’ The ‘Bosch-etch’ process involves applying a negative potential to the wafer while cycling SF₆ gas and C₄F₈ gas over the silicon surface. The photo-resist pattern of the islands from
Fig. 2.14 TEM image of a Ti/Nb atom probe tip with the layered stacking normal to the direction of field evaporation.
**Fig. 2.15** Atom probe specimen preparation steps for multilayered thin films: (a) 5 µm x 5 µm x 60-80 µm Si post that have been ‘Bosch-etched.’ The islands provide the substrate for the deposited multilayer (b) The deposited film on the Si posts are fractured from the Si wafer generating thousands of potential specimens (c) Lightly applying silver epoxy to the fine tipped metal pin (d) A Si post with identifiable ends for retrieval. (e) Retrieval and attachment of a Si post to the metal tip using silver epoxy. Parallel alignment of the Si post to the metal tip using a glass rod. (f) The aligned Si post to the needle tip ready for FIB milling
the previous photolithography steps allows specific regions on the wafer surface to be etched while other regions are protected. The ionization of the gas allows the fluoride ions to attack and etch away the silicon. To achieve a high aspect ratio, the $C_4F_8$ gas cycles in between etches and applies a protective polymer coating to the side-wall of the freshly etched Si trenches. As shown in Fig. 2.15(a), after etching a series of $5 \mu m \times 5 \mu m \times 60-80 \mu m$ pillars remain on the Si surface. The Si wafer is then oxygen ion etched to remove the protective polymer resist from the surface and pillar trench’s side-walls of the Si substrate. The wafer, with pillars, is then used as the substrate for the growth of the desired multilayered film.

Once the multilayered film is deposited onto the top of the substrate pillars, the pillars’ bases were then mechanically fractured from the wafer using a surgical scalpel as seen in Fig. 2.15(b). A fine tipped stainless steel biological pin, mechanically attached to a copper tube, was electropolished in a 80% phosphoric acid bath to remove the native oxide from the surface. Using a micro-manipulator, the tip of the metal pin was dipped into a silver epoxy, as shown in Fig. 2.15(c), and used to retrieve the Si post as shown in Fig. 2.15(e). To distinguish which end of the Si post contained the multilayer, only fractured posts that could be distinguished with a flat surface (film) and a fractured angled surface were used (Fig. 2.15(d)). Once the post was plucked and attached to the needle tip, it was aligned to be parallel with the tip, as seen in Fig. 2.15(f), using a glass rod. Once aligned, the silver epoxy was cured at 80°C for one hour.

The atom probe Si post with needle and Cu tube were mechanically clamped onto a stub and placed into an FEI DB-235 Focus Ion Beam instrument. Once the Si post was aligned in the FIB, a $1.5 \mu m \times 1.5 \mu m \times 2.0 \mu m$ Pt surface layer was deposited on the
Fig. 2.16 (a) Alignment of post to Ga ion source. (b) Pt sacrificial layer placed onto of the film/Si post prior to FIB milling (c) Initial annular milling of the specimen (d) Annular milling of the specimen into a fine tipped post. The Si, multilayer film, and Pt cap layers are clearly visible. (e) TEM bright-field image of the final milled tip.
surface, as shown in Fig. 2.16(b), to serve as sacrificial protective layer during milling.

Without this protective surface layer, ion implantation could generate intermixing and possible embrittlement of the specimen. The specimen tip was then annular ion milled in steps with an inner radius of 1.5 \(\mu\)m at 500 pA, 0.7 \(\mu\)m at 300-500 pA, and 0.15 \(\mu\)m at 100 pA using 30 keV Ga ions. As shown in Fig. 3.16(b), the outer radius of the concentric milling circle was set to encompass the entire planar surface of the Si post such that only a needle tip would be left. Since the Ga ion beam has an energy tail near the edge of designated inner radius limit, subsequent milling passes form a tapered angle to the post such that the tip is milled into the desired radius. As milling proceeds to form a thinner and thinner needle tip, a lack of contrast between the Si substrate, the multilayer, and the Pt layer develops. In order to not over-mill and remove the multilayer film, a visual measurement bar is placed on the last discernable electron beam image of the Pt-multilayer interface on the DB-235 SEM screen. The DB-235 electron image is 52° off-set from the normal Ga ion milling direction. In this imaging orientation, it is possible to have a pseudo-cross-section image of the specimen while ion milling. As the tip decreases in size, the Pt layer is eventually milled way. When the tip’s apex reaches the Pt-multilayer interface, designated by a line on the FIB SEM screen, milling should be manually stopped and, ideally, the tip’s apex is the multilayer which has not been milled. Even though the sides of the tip have experienced Ga ion milling damage, which is usually 2-5 nm in thickness, the atom probe collection is taken from a smaller region in the middle of the tip that is far from the damaged side-walls. The specimens were then carefully removed and stored under static vacuum until atom probe analysis. Results are discussed in Chapter 4.
2.6 Functional Properties

Phase stability of the nanostructured thin films could have marked influences on the properties of the films. This was briefly addressed with the example of the magnetic property changes observed in pseudomorphic phases in Chapter 1’s Section 1.1. The electronic transport and the elastic modulus of the Zr/Nb multilayers were investigated.

2.6.1 Superconductivity

Upon cryogenic cooling of the Zr/Nb multilayers to temperatures near 9 K, the multilayer can become superconductive. Lowe and Gabelle [30] have reported an enhancement of the critical transition temperature, \( T_c \), for a 1.55 nm \( bcc \) Zr / 1.55 nm \( bcc \) Nb multilayer. Lowe and Gabelle contributed the enhancement of the \( T_c \) to be the formation of a solid-solution of Zr-Nb at the interface. To establish if other similar phase stability changes, as a function of volume fraction, could exhibit marked changes in \( T_c \), a series of magnetization verses temperature experiments have been performed on the Zr/Nb multilayers.

As a superconductor is cooled below its \( T_c \), it becomes diamagnetic. Diamagnetism is the expulsion of an external magnetic field from the interior of a superconductor. This change in the magnetization state with temperature was used to determine the superconducting transition temperature using a Quantum Design Magnetic Property Measurement System (MPMS) SQUID, with a minimum temperature of 1.8 K, shown in Fig. 2.17(a) and Fig. 2.17(b). The superconducting \( T_c \) experiments were performed at the Department of
Fig. 2.17 (a) Quantum Design Magnetic Property Measurement System (MPMS) SQUID used for $T_c$ measurements. (b) Illustration of the magnetization measurement coil used to determine when a specimen has become superconductive
2.6.2 Nanoindentation

By indenting a surface with a diamond tip and measuring the load and displacement simultaneously, useful mechanical property responses can be measured. This is particularly meaningful in establishing if and how much the elastic modulus is altered by a change in phase stability. Using a MTS NanoIndentor, similar to the schematic diagram of figure 2.18(a), the modulus for the Zr/Nb films was measured. The MTS NanoIndentor uses a 3-faced Berkovich diamond tip fasted to a leaf spring that is compliant in the loading direction and stiff in the transverse direction to test the mechanical response of the specimens. As the diamond tip is moved towards the surface, a capacitance displacement gauge, with resolution near 4 Å, monitors the total displacement. The applied load on the tip can be varied from 0.25 μN to 120 mN. The Zr/Nb multilayers were run with a depth displacement protocol such that the load response was in relationship to the final indent depth.

Fig. 2.18(b) is a typical nanoindentation load, $P$, verses displacement, $h$, curve. Both elastic and plastic deformation occurs during nanoindentation [32-33]. Using the slope of the unloading curve, given in Eq. (2.14), the elastic modulus of the material can be determined by [32]

$$S = \frac{dP}{dh} = b \cdot E^* \cdot (A)^{1/2} \quad (2.14)$$
Fig. 2.18 (a) A schematic diagram of a nanoindentor [32] (b) A typical nanoindentation load, P, verses displacement, h, curve [33].
where $S$ is the slope of the unloading curve which is equal to the change in $P$ (load) to the change in $h$ (depth of indentation), $A$ is the contact area, $b$ is a constant that depends on the shape of the indentor, and $E^*$ is the effective modulus. The effective modulus is defined as
\[
\frac{1}{E^*} = \frac{(1-\nu_o^2)}{E_o} + \frac{(1-\nu^2)}{E}
\]  
(2.15)

where $E_o$ and $\nu_o$ are Young’s modulus and Poisson’s ratio of the indentor and $E$ and $\nu$ are Young’s modulus and Poisson’s ratio for the material being indented. The Poisson ratio of the material being indented was taken to be a simple average of Zr and Nb.

Since nanoindentation of thin films occurs on substrates, it is critical to be able to separate the contribution of the substrate from the film. To determine the modulus of a film on a substrate, Doerner and Nix [34] showed that the product of the compliance and the film thickness uniquely depended upon the ratio of the total film thickness to the effective depth of indentation. Ideally, nanoindentation data should be taken from a thickness range less than 10% the total film thickness. Data collected from indentation depths need to commence no earlier than 20 nm. Data prior to this depth level can be unreliable due to surface impurities and imperfections in the tip’s contact area. Imperfections on the nanoindentor tip’s area are significantly more pronounced for a smaller contact area in the initial stages.

The Zr/Nb multilayers grown in this study were sputtered deposited to a total thickness range of 350 nm – 600 nm. In order to avoid significant artifacts from the Si substrate as well as provide sufficient contact area within the film for an accurate measurement, mechanical response data was collected in the 20 nm – 40 nm range. The multilayers were mounted and secured into place on aluminum blocks using a low-temperature melting epoxy (Crystal-Bond). The films’ surfaces were cleaned with a rinse of acetone and methanol. If a
surface film from the rinse developed, the specimen was re-rinsed and dried until the surface appeared clear (mirror reflection). The alumni blocks were then fixtured into the specimen tray to the appropriate sample height using a granite leveling block. Once the blocks were mounted, an automated nanoindentation run, using the XP NanoIndentor head, was started using the parameters listed in Table 2.2. Prior to indenting the specimen, the XP indentor tip was indented into aluminum 5 separate times to clean the tip’s surface and then indented 10 separate times into fuse silica to accurately calibrate the tip’s surface area for the penetration depths used. Chapter 5 contains the experimental results and discussion.

<table>
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<tr>
<th>Drift Rate</th>
<th>&lt;0.02 nm/sec.</th>
</tr>
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<tr>
<td>Poisson ratio</td>
<td>simple average of the two materials Zr/Nb ~ 0.389</td>
</tr>
<tr>
<td># of indents</td>
<td>25 per sample</td>
</tr>
<tr>
<td>Indent spacing</td>
<td>5 μm x 5 μm</td>
</tr>
</tbody>
</table>

**Table 2.2** Nanoindentor run parameters.
References for Chapter 2

CHAPTER 3

PSEUDOMORPHIC PHASE STABILITY IN ZIRCONIUM / NIOBIUM MULTILAYERS

3.1 Zr/Nb Multilayers

The bulk equilibrium structures of Zr and Nb are hcp and bcc respectively [1]. As stated in the introduction chapter, pure elemental Zr exhibits an allotropic transformation from the hcp α-Zr phase to the bcc β-Zr at a temperature of 1113 K at 1 atm. [2]. Stabilization of a bcc phase in the Zr layers of sputter deposited Zr/Nb multilayers at room temperature has been reported by Lowe and Geballe [3]. In their work, a series of multilayers, with a varying bilayer thickness, \( \lambda \), but with the same overall composition of 50 % Zr / 50 % Nb were characterized using x-ray diffraction. Their results reveal that when the bilayer spacing was reduced below \( \approx 3.1 \) nm (1.55 nm Zr / 1.55 nm Nb), the bulk hcp Zr / bcc Nb structure transformed to a pseudomorphic coherent bcc Zr / bcc Nb structure. Lowe and Geballe [3] did not vary the volume fraction of the constituent layers in their multilayers. Based upon the classical thermodynamic model proposed by Dregia et al. [4], additional hcp to bcc Zr phase stability transitions, as a function of bilayer spacing and volume fraction, should exist for Nb-rich bilayers. Furthermore, could the Zr/Nb multilayer exhibit a region of hcp Nb phase stability in extreme Zr-rich bilayer volume fractions? In the sections below, the
classical thermodynamic model, for the first time, has been used to systematically predict, and not serendipitously discover, pseudomorphic phase stability in Zr/Nb multilayers.

3.2 Predicting bcc Zr Phase Stability

Using the classical thermodynamic model [4] in Chapter 1, the Zr/Nb bilayer unit’s free energy change per unit of interfacial area, $\Delta g$, accompanying a structural transition is given as

$$\Delta g = 2\Delta \gamma + \Delta G_{Nb}f_{Nb}\lambda + \Delta G_{Zr}(1 - f_{Nb})\lambda$$

(3.1)

where $\Delta g$ is the interfacial free energy difference between a bcc Zr / bcc Nb and a hcp Zr / bcc Nb interface, $\Delta G_i$ is the allotropic volumetric free energy change for component $i$, $f_{Nb}$ is the volume fraction of Nb, and $\lambda$ is the bilayer spacing. Eq. (3.1) provides the basic thermodynamic framework for representing phase stability in Zr/Nb multilayers. Obviously other terms, such as strain energy, can contribute to $\Delta g$. In order to maintain simplicity in this initial approach, it is assumed that all energetic contributions that scale with the volume are contained within the $\Delta G_i$ term and all energetic contributions that scale with the interfacial area are contained in the $\Delta g$ term. In subsequent sections, the addition of strain energy to Eq. (3.1) will be applied.

Coupling Eq. (3.1) to the original transformation point by Lowe and Geballe [3], a proposed biphase diagram has been constructed and can be viewed in Fig. 3.1. The single structural transition from hcp Zr to bcc Zr for $\lambda < 3.1$ nm at a $f_{Nb} = 50$ at.% has been indicted on Fig. 3.1 as an open circle. Based on this data point, a biphase stability boundary separating
Fig. 3.1 Proposed biphase stability diagram for hcp to bcc phase stability in Zr for Zr/Nb multilayers. The biphase stability boundary is based upon the single hcp to bcc transition, represented by the open circle, reported by Lowe and Geballe [3].
the regions of $hcp$ Zr / $bcc$ Nb and $bcc$ Zr / $bcc$ Nb can be predicted. The boundary is initially assumed to be a straight line. This assumption is equivalent to ignoring the effects of coherency strains [4]. The thermodynamics dictates that this biphase boundary line, drawn through the transition point at $f_{Nb}=0.5$, must approach $1/\lambda = 0$ as $f_{Nb}$ approaches 1. Thus, as the volume fraction of Nb is increased, the critical value of $\lambda$ at which the transition occurs increases. By setting $\Delta g = 0$ and reorganizing the terms of Eq. (3.1), the slope of this biphase boundary is given as

$$slope = \Delta G_{Zr} / (\gamma_{bcc} / bcc - \gamma_{bcc} / hcp)$$

(3.2)

and would be a negative value. $\Delta G_{Nb}$, in Eq. (3.1), is zero since it does not experience a change in phase stability between the two biphase stability fields. The slope, being a constant, indicates that the thickness of an individual Zr layer ($= \lambda(1 - f_{Nb})$) will remain a constant along the boundary.

### 3.2.1 Effect of Coherency Strains on the Biphase Diagram

The biphase diagram shown in Fig. 3.1 has been constructed using a simplifying assumption that the $\Delta G_i$ and $\Delta g$ terms are independent of $f_{Nb}$ and $\lambda$. This would not be the case for multilayers that experience coherency strains, where the equilibrium coherency is inversely proportional to its thickness [5]. If coherency strain energy were included in the thermodynamics, $\Delta g$ would depend non-linearly on volume fraction and lead to curved boundaries in $1/\lambda$ vs. $f_{Nb}$ space. This strain energy term can be simply added as an addition contribution to Eq. (3.1). For a coherently strained unit Zr/Nb bilayer [6], the strain energy per unit area of interface is given by
\[ W_{el} = \left[ Y_{Nb} \varepsilon_{Nb}^2 f_{Nb} + Y_{Zr} \varepsilon_{Zr}^2 (1 - f_{Nb}) \right] \lambda \]  

(3.3)

where, for each metal, \( Y \) is a biaxial elastic modulus and \( \varepsilon \) is the coherency strain. The natural misfit is partitioned such that \( |\varepsilon_{Nb}| + |\varepsilon_{Zr}| = m \), and for force balance, \( (Y_{ef}\lambda)_{Nb} + (Y_{ef}\lambda)_{Zr} = 0 \). Thus, both \( \varepsilon_A \) and \( \varepsilon_B \) can be expressed in terms of \( m \), and Eq. (3.3) becomes

\[ W_{el} = Ym_0^2 \]  

(3.4)

with

\[ Y = \frac{Y_{Nb}Y_{Zr}f_{Nb}(1 - f_{Nb})}{Y_{Nb}f_{Nb} + Y_{Zr}(1 - f_{Nb})} \]  

(3.5)

Inserting \( W_{el} \) into Eq. (3.1), the total free energy of formation of a coherent Zr/Nb unit bilayer is then given as

\[ \Delta g_c = 2\Delta \gamma_c + \left[ \Delta G_{Nb} f_{Nb} + \Delta G_{Zr} (1 - f_{Nb}) + Ym_0^2 \right] \lambda \]  

(3.6)

### 3.3 bcc Zr Results

Using the proposed Zr/Nb biphase diagram of Fig. 3.1 as a guide, a series of multilayered films have been sputtered deposited and are listed in Table 3.1. A group of these data points between \( f_{Nb} = 0.4 \) to 1.0 have been plotted in Fig. 3.2. Figs. 3.3(a) and 3.3(b) are representative Zr/Nb TEM plan-view and cross-section bright-field many-beam micrographs. In the cross-section, it is evident that the films exhibited morphologically sharp interfaces. Results of both XRD and plan-view electron diffraction indicated that the multilayers’ crystal structures were commensurate with their locations in the phase stability fields predicted by the proposed biphase diagram of Fig. 3.1. The transmission XRD
Fig. 3.2 Series of Zr/Nb multilayers deposited at various bilayer thicknesses and volume fractions. The phases of the multilayers was commensurate with the predicted boundary of Fig. 3.1.
**Fig. 3.3** (a) Plan-view bright-field electron micrograph which is representative of the deposited Zr/Nb multilayers. The film is polycrystalline. (b) Cross-section bright-field electron micrograph of a representative Zr/Nb multilayer. The interfaces are morphologically sharp.
Fig. 3.4 (a) Transmission XRD pattern for the Zr/Nb multilayer #1 in Fig. 3.2. The multilayer diffracts the *hcp* Zr and the *bcc* Nb phases (b) Transmission XRD pattern for the Zr/Nb multilayer #2 in Fig. 3.2. The pattern was indexed to a *bcc* Zr and *bcc* Nb phase.
diffraction patterns in Figs. 3.4(a) and 3.4(b) correspond to those multilayers (marked #1 and #2 on Fig. 3.2) on either sides of the biphase boundary between \( hcp \ Zr / bcc \ Nb \) – \( bcc \ Zr / bcc \ Nb \) phase fields. It is clearly evident that \( hcp \ Zr \)’s \{10\bar{1}0\} intensity is no longer present in Fig. 3.4(b) as compared to Fig. 3.4(a). As the bilayer thickness was reduced for a fixed volume fraction of Nb, the Zr layer within the Zr/Nb bilayer has undergone a change in phase stability.

These results were confirmed by plan-view electron diffraction. Fig. 3.5(a) is the plan-view electron diffraction pattern of the #1 data point in Fig. 3.2. It was consistently indexed as \( hcp \ Zr \) and \( bcc \ Nb \). This is in complete agreement with the transmission XRD pattern of Fig. 3.4(a). Fig. 3.5(b) is the plan-view electron diffraction pattern of the #2 data point in Fig. 3.2. It was consistently indexed as \( bcc \ Zr / bcc \ Nb \) and in agreement with the transmission XRD pattern of Fig. 3.4(b). The use of plan-view electron diffraction as a legitimate technique for phase identification as outlined in Chapter 2 Section 2.4.3 has been additionally confirmed through the comparison of the transmission XRD and plan-view electron diffraction patterns for these multilayers. Fig. 3.5(c) is the plan-view electron diffraction pattern for the #3 multilayer labeled on Fig. 3.2. The breadth of the ring is due to the small grain size exhibited by this particular multilayer.

A line scan intensity profile of the two inner electron diffraction rings of Fig. 3.5(a) is shown in Fig. 3.6(a). A similar line intensity profile for the inner ring of Fig. 3.5(b) is shown in Fig. 3.6(b). Careful observation of Fig. 3.6(b) of \( bcc \ Zr / bcc \ Nb \) multilayer #2 shows a smearing of the \{110\} \( bcc \) intensity. The intensity line scan profile of this ring indicates the asymmetry. This intensity profile has been deconvoluted using Gatan Digital
Fig. 3.5 (a) Plan-view electron diffraction pattern for the Zr/Nb multilayer #1. The pattern is consistently indexed to a hcp Zr and bcc Nb phase (b) Plan-view electron diffraction pattern for the Zr/Nb multilayer #2. The pattern is consistently indexed as bcc Zr and bcc Nb (c) Plan-view electron diffraction pattern for the Zr/Nb multilayer #3. This pattern is consistently indexed as bcc Zr and bcc Nb. The breath of the rings’ intensity is due to the relative small grain size for this particular multilayer.
Micrograph imaging process software and has been interpreted on the basis of two \{110\} reflections, one from \textit{bcc} Nb and the other from \textit{bcc} Zr. The interplanar spacings for these has two rings indicated that Zr’s \textit{bcc} lattice parameter value is 3.54 Å; this lattice parameter is within 1.2\% of the lattice parameter of \textbeta{}-Zr extrapolated from high temperatures to room temperature [7]. Nb retained its bulk lattice parameter value of 3.30 Å. The \textit{bcc} Zr phase has formed a semi-coherent \textit{bcc}/\textit{bcc} interface with Nb that is essentially strain-free. Upon further reduction of \(\lambda\), the Nb/Zr interfaces became coherent. This is indicated in Fig. 3.6(c) by the symmetric intensity distribution in the \{110\} diffracted intensity.

A similar result of a semi-coherent to coherent transformation of \textit{bcc} Zr was seen for a set of plan-view electron diffraction patterns for multilayers grown at \(f_{\text{Nb}} = 0.5\). These data points are labeled #4, #5, and #6 in Fig. 3.2 and whose phase structure is tabulated in Table 3.1. The larger volume fraction of Zr has allowed the \textbeta{}-Zr line intensity profile to be more clearly evident in Fig. 3.7(b) from its plan-view electron diffraction pattern in Fig. 3.7(a). Figs. 3.7(c) and 3.7(d) are the plan-view diffraction pattern and line intensity profile of Zr/Nb multilayer #6. Again, the breath of the ring is due to the relatively small grain size for this particular multilayer.

The #6 Zr/Nb multilayer being coherent at a lower bilayer spacing then Lowe and Geballe’s [3] original data point used in the prediction of Fig. 3.1 is believed to be due to the quality of the interfaces. As will be shown and discussed in Chapter 5, the multilayers grown in this study have exhibited properties suggestive of a more abrupt interface than those grown by Lowe and Gabelle [3]. Lowe and Gabelle [3] have indicted in their work of
Fig. 3.6 (a) A line intensity profile of the two inner ring of Fig. 3.5(a). The \{10\bar{1}0\} hcp Zr and \{110\} bcc Nb intensities are present (b) A line intensity profile of the inner rings of Fig. 3.5(b). The \{10\bar{1}0\} hcp Zr ring is no longer present. The \{110\} bcc Nb intensity is asymmetric and has been indexed based upon two bcc Nb lattice parameters, bcc \(\beta\)-Zr and bcc Nb (c) A line intensity profile of the inner ring of Fig. 3.5(c). The \{110\} intensity is symmetric indicating coherency of the two bcc phases.
Fig. 3.7 (a) Plan-view electron diffraction pattern for Zr/Nb multilayer #5 in Fig. 3.2. The pattern was consistently indexed as the \textit{bcc} phases for Zr and Nb (b) Line intensity profile of the inner ring of (a). The asymmetry of the \{110\} intensity has been indexed as \textit{bcc} $\beta$-Zr and \textit{bcc} Nb (c) Plan-view electron diffraction pattern of the Zr/Nb multilayer #6. The pattern has been indexed as a coherent \textit{bcc} Zr / \textit{bcc} Nb multilayered structure (d) Line intensity profile of the \{110\} intensity. The peak is symmetric indicating coherency of the two phases in plane.
<table>
<thead>
<tr>
<th>Phase (Zr/Nb)</th>
<th>$\lambda$(nm)</th>
<th>$f_{\text{Nb}}$</th>
<th>EDS$_{\text{Nb}}$ (at.%)</th>
<th>Sputt.Pwr (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 hcp/bcc</td>
<td>9.2</td>
<td>0.79</td>
<td>84</td>
<td>200</td>
</tr>
<tr>
<td>#2 bcc-β/bcc</td>
<td>7.0</td>
<td>0.86</td>
<td>87</td>
<td>200</td>
</tr>
<tr>
<td>#3 bcc/bcc</td>
<td>4.5</td>
<td>0.88</td>
<td>90</td>
<td>25</td>
</tr>
<tr>
<td>#4 hcp/bcc</td>
<td>5.2</td>
<td>0.38</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>#5 bcc-β/bcc</td>
<td>3.6</td>
<td>0.47</td>
<td>52</td>
<td>100</td>
</tr>
<tr>
<td>#6 bcc/bcc</td>
<td>2.4</td>
<td>0.46</td>
<td>51</td>
<td>25</td>
</tr>
<tr>
<td>#7 hcp/bcc</td>
<td>5.6</td>
<td>0.71</td>
<td>76</td>
<td>200</td>
</tr>
<tr>
<td>#8 bcc/bcc</td>
<td>2.3</td>
<td>0.64</td>
<td>68</td>
<td>100</td>
</tr>
<tr>
<td>#9 hcp/bcc</td>
<td>5.1</td>
<td>0.19</td>
<td>24</td>
<td>100</td>
</tr>
<tr>
<td>#10 hcp/hcp</td>
<td>3.5</td>
<td>0.29</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>#11 hcp/hcp</td>
<td>2.2</td>
<td>0.26</td>
<td>31</td>
<td>60</td>
</tr>
<tr>
<td>#12 hcp/hcp</td>
<td>5.0</td>
<td>0.12</td>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 3.1** Deposited Zr/Nb multilayers
a *bcc* solid-solution formation at the interface with an approximate thickness of 1nm. This intermixing may help facilitate coherency at larger bilayer spacings.

XRD scans indicated that the bulk equilibrium phases of Zr and Nb grew in a texture orientation associated with their closest pack direction, e.g. \{011\} and \{0002\} respectively. For extremely thick bilayers of 500 nm *hcp* Zr / 500 nm *bcc* Nb, the Zr showed the presence of a \{1010\} peak along with the \{0002\}. As discussed in detail in Chapter 1, surface energies and faceting directions can be altered with continual thickening of the film. For the propose of this research, multilayers studied had $\lambda < 15$ nm and only exhibited the \{011\} and \{0002\} textures.

Coupling the XRD results for the films along with the electron diffraction results from plan-view TEM specimens, a Burgers or near-Burgers orientation relationship between the *bcc* Nb and *hcp* Zr phases is reported. The Burgers orientation relationship is defined as

\[
\begin{align*}
\{011\}_{bcc} &// \{0001\}_{hcp} \\
<111>_{bcc} &// <1\bar{1}20>_{hcp}
\end{align*}
\]

Upon transformation to *bcc* Zr, the orientation relationship with *bcc* Nb became

\[
\begin{align*}
\{011\}_{bcc} &// \{011\}_{bcc} \\
<111>_{bcc} &// <111>_{bcc}
\end{align*}
\]

### 3.4 Discussion on *bcc* Zr Phase Stability

Using a previous reported experimental data point for the change in phase stability of *hcp* Zr to *bcc* Zr in Zr/Nb multilayers, and a classical thermodynamics model, a biphase diagram has been constructed. Subsequently, a whole series of Zr/Nb multilayers with
different values of \( f_{Nb} \) and \( l \) have been deposited on the Nb-rich side of the biphase diagram.

The results of structural characterization of these multilayers are in agreement with the predictions afforded by the proposed biphase diagram. The experimental results clearly indicate that on reducing \( \lambda \) at a constant \( f_{Nb} \), the structural transformation from \( hcp \) to \( bcc \) Zr occurs prior to the formation of a coherent \( bcc \) Zr / \( bcc \) Nb interface. The adoption of independent lattice parameters (negligible coherency strains) allows for a linear boundary to be drawn for the initial biphase stability boundary. But it also appears that in addition to this boundary between \( hcp \) Zr / \( bcc \) Nb and \( bcc \) Zr / \( bcc \) Nb, there exists a second boundary between semi-coherent \( bcc \) \( \beta \)-Zr / \( bcc \) Nb and coherent \( bcc \) Zr / \( bcc \) Nb. The slopes of these biphase boundaries may be used to deduce information concerning the energetics associated with the phase stability of \( hcp \) and \( bcc \) Zr.

### 3.4.1 Biphase Boundaries and Associated Interfacial Energies

As discussed earlier, the equation of the biphase boundary is obtained by equating \( \Delta g \)’s of the two relevant biphases. In the absence of coherency strains, the relevant \( \Delta g \)’s are represented by Eq. (3.1) and the location of the biphase boundary is then given by

\[
\frac{1}{\lambda} = \frac{-\Delta G_{Zr}}{2(\gamma_{bcc/bcc} - \gamma_{bcc/hcp})}(1 - f_{Nb})
\]

(3.7)

with the slope of the biphase boundary being

\[
\frac{\Delta G_{Zr}}{2(\gamma_{bcc/bcc} - \gamma_{bcc/hcp})}
\]

(3.8)

Using the experimental results, the slope of the biphase boundary has been determined from Fig. 3.2. The bulk free energy change per unit volume when Zr transforms from \( hcp \) to
bcc, as computed using solution thermodynamics based models such as CALPHAD, is \( \Delta G_{Zr} = 3.7 \times 10^8 \text{ J/m}^3 \) \[8\]. A simple average of the atomic volumes for hcp Zr (13.5x10^{-6} \text{ m}^3/\text{mol}) and bcc Zr (13.4x10^{-6} \text{ m}^3/\text{mol}) was used in the conversion of the volumetric free energy difference from energy per moles to energy per volume in order to compare it to the slope. Substituting \( \Delta G_{Zr} \) into Eq. (3.6) yielded

\[
\Delta \gamma_{\text{exp}} = \gamma_{\text{bcc/bcc}} - \gamma_{\text{bcc/hcp}} = -250 \text{ mJ/m}^2.
\]

A number of different factors contribute towards \( \Delta g \) including a chemical and a structural contribution \[9\]. The chemical component arises from the change in bonding across the interface while the structural component arises from the change in misfit at the interface accompanying the change in phase. The structural component of \( \Delta \gamma \), \( \Delta \gamma_{\text{struc}} \), can be evaluated based on the difference in the line energy per unit interfacial area between the misfit dislocation networks for a semi-coherent bcc \( \beta \)-Zr / bcc Nb and a hcp Zr / bcc Nb interface, i.e.

\[
\Delta \gamma_{\text{bcc/bcc}} = \gamma_{\text{bcc/bcc}}^\perp - \gamma_{\text{bcc/hcp}}^\perp
\]

where \( \gamma_{\perp} \) is the line energy per unit area of misfit dislocations at the interface.

To calculate a first approximation to the structural component of the interfacial energies, the Bollman’s O-lattice \[10-11\] approach to modeling a misfit dislocation networks has been adopted. An O-lattice is a mathematical construction of a third ‘virtual’ lattice that is formed by the superposition of two other lattices. The O-lattice’s O-points represent lattice positions that are common between the two reference lattices. In a physical setting, O-points represent points of best fit between two independent lattices and areas halfway between O-points represent places of least-fit. These least-fit areas can be used to indicate
where dislocations would be located. By constructing various dislocation networks around these areas, the network with the minimal energy can be used to approximate the true dislocation network contribution to the structural component of the interfacial energy. Furuhara and Aaronson [12] have shown studies in which reasonable agreement can be obtained from the calculated and experimental values of the O-lattice network to that observed in α/β interfaces. Perovic and Weatherly [13-15] have extensively studied the α/β interfaces in binary Zr-rich Zr-Nb alloys. A complex dislocation network consisting of <a> and <a+c> dislocations have been experimentally observed at the α/β interfaces when these two phases exhibit the Potter orientation relationship:

{011}_β // {1011}_α

<111>_β // <1210>_α

In case of the Zr / Nb multilayers being investigated in the this study, the Burgers orientation relationship, rather than the Potter relationship, was observed for the hcp Zr / bcc Nb interface. A two-dimensional centered rectangular lattice was constructed for the {0001} basal plane of Zr [16] in contact with the {011} plane of Nb in the Burgers or near-Burgers orientation relationship. To maintain a simple two-dimensional interface, only <a> type dislocations were used to construct the network. The Burgers vector for this network is of the type \( \mathbf{b} = 1/3 <2\bar{1}0> \) (with reference to the hcp Zr layer). Fig. 3.8(a) is a schematic representation of the assumed dislocation network based on the O-lattice approach. This dislocation array has been commonly observed in other α/β interfaces that exhibited the Burgers orientation relationship [12]. As seen in Fig. 3.8(a), the Burgers vectors are neither parallel nor perpendicular to the dislocation lines but are inclined at a certain angle. Using
the equation by Matthew [17], the energy per unit length of a misfit dislocation line segment between two isotropic solids is

\[
E_l = \frac{\mu_{Nb}\mu_{Zr}b^2}{2\pi(\mu_{Nb} + \mu_{Zr})} \frac{1 - \nu \cos^2 \alpha}{(1 - \nu)} (\ln h/b + 1)
\]  

(3.10)

where \(\mu\) and \(\nu\) denote shear modulus and Poisson’s ratio, \(b\) is the length of the Burger’s vector of the misfit dislocations, \(\alpha\) is the angle between the Burgers vector and the dislocation line, and \(h\), for this case, being the layer thickness of the Zr layer. \(\nu\) was taken to be the average of Nb’s 0.397 and Zr’s 0.38 Poisson’s ratio [18]. The shear moduli of bcc Nb and hcp Zr used in the calculation are 37.5 GPa and 35.5 GPa respectively [18]. With the aid of Eq. (3.10), the energy per unit length for the two sets of misfit dislocations, \(E_{l1}\) and \(E_{l2}\), corresponding to the angles \(\alpha_1\) (49.6°) and \(\alpha_2\) (10.4°), has been calculated. The energy per unit interfacial area is

\[
\gamma_{bcc/hcp} = \frac{E_{l1}l_1 + E_{l2}l_2}{l_1l_2 \sin \theta}
\]  

(3.10)

where \(l_1\) and \(l_2\) are the length of dislocation line segments (≈ 7.7 nm each) in an unit cell of the network and \(\theta\) (20.8°) is the angle between \(l_1\) and \(l_2\). This calculation yields a value of \(\gamma_{bcc/hcp} \approx 500 \text{ mJ/m}^2\)

A similar 2-dimensional O-lattice lattice with in-plane dislocations of the type \(b = a<100>\) and \(a/2<111>\) was constructed for modeling the misfit at the bcc Zr / bcc Nb interface. Fig. 3.8(b) is a schematic representation of the resulting hexagonal network of pure edge dislocations for the bcc / bcc interface. The shear modulus of bcc Zr used for the calculation was 17 GPa [19] and the length of the dislocation segments, \(l_1\) and \(l_2\), predicted by the O-
Fig. 3.8 (a) 2-dimensional O-lattice dislocation network for the hcp Zr / bcc Nb interface (b) 2-dimensional O-lattice dislocation network for the bcc β-Zr / bcc Nb.
lattice construction, was 1.8 nm and 3.0 nm respectively. The estimated dislocation line energy per unit area from Eq. (3.11) was found to be $\gamma_{\text{bcc}}/\text{bcc} \approx 140 \text{ mJ/m}^2$.

Using these o-lattice values, a calculated $\Delta \gamma$ for the transformation was acquired by

$$\Delta \gamma_{\text{bcc}}/\text{bcc} = \gamma_{\text{bcc}}/\text{bcc} - \gamma_{\text{bcc}}/\text{hcp} = -360 \text{ mJ/m}^2.$$  
This difference in dislocation line energies is larger than the interfacial energy difference experimentally obtained from the slope, e.g. $\approx -250 \text{ mJ/m}^2$. Subsequently the driving force for transformation could be completely driven by the reduction in the structural misfit dislocation line energies between the two systems.

The chemical component of the interfacial free energy was estimated using a simple nearest-neighbor bond model. In this approach, the interfacial energy for a perfectly coherent $\text{bcc} / \text{bcc}$ or $\text{hcp} / \text{hcp}$ interface can be estimated in terms of the binary solution thermodynamics interaction energy, $\omega$,

$$\omega_{\text{hcp}}^{\text{Nb-Zr}} = \phi_{\text{hcp}}^{\text{Nb-Zr}} - 1/2(\phi_{\text{hcp}}^{\text{Nb-Nb}} + \phi_{\text{hcp}}^{\text{Zr-Zr}})$$  
where $\phi_{A-B}^{\text{hcp}}$ is the bond energy for the A-B bond in the hcp structure [20]. An equivalent definition holds for $\omega_{\text{bcc}}^{\text{Nb-Nb}}$. $\omega$ is related to the regular solution parameter, $\Omega$, by the relationship $\Omega = Z\omega$, where $Z$ is the coordination number. For a (011) $\text{bcc Nb} / \text{bcc Zr}$ interface, the excess energy per atom (with respect to the bulk) on the Nb side equals $\Delta E_{\text{atom}}^{\text{Nb}} = 2\phi_{\text{Nb-Zr}}^{\text{hcp}} - 2\phi_{\text{Nb-Nb}}^{\text{hcp}}$ while the excess energy per atom on the Zr side equals $\Delta E_{\text{atom}}^{\text{Zr}} = 2\phi_{\text{Nb-Zr}}^{\text{hcp}} - 2\phi_{\text{Zr-Zr}}^{\text{hcp}}$. Therefore, the chemical component of the interfacial energy per atom ($\gamma_{\text{chem}}^{\text{atom}}$) can be approximated as follows:

$$\gamma_{\text{chem}}^{\text{atom}} = (\Delta E_{\text{atom}}^{\text{Nb}} + \Delta E_{\text{atom}}^{\text{Zr}})/2 = 2[\phi_{\text{Nb-Zr}}^{\text{hcp}} - 0.5(\phi_{\text{Nb-Nb}}^{\text{hcp}} + \phi_{\text{Zr-Zr}}^{\text{hcp}})]$$

$$= 2\omega_{\text{hcp}}^{\text{Nb-Zr}} = 0.25 \Omega_{\text{hcp}}^{\text{Nb-Zr}}$$  
(3.13)
Based on a recent assessment of the Nb-Zr binary phase diagram [8], \( \Omega_{\text{Nb-Zr}}^{\text{bcc}} = 2.8 \times 10^{-20} \text{ J/atom} \); therefore, \( \gamma_{\text{atom}}^{\text{chem}} = 7 \times 10^{-21} \text{ J/atom} \). Multiplying with the number of atoms per unit area on the (011) bcc plane, \( \gamma_{\text{atom}}^{\text{chem}} \approx 91 \text{ mJ/m}^2 \). Using an equivalent nearest-neighbor approximation and a value of \( \Omega_{\text{Nb-Zr}}^{\text{hcp}} = 4.1 \times 10^{-20} \text{ J/atom} \) [8], \( \gamma_{\text{atom}}^{\text{chem}} \approx 44 \text{ mJ/m}^2 \). The difference in the number of out-of-plane bonds between the (011) bcc plane (2 bonds) and the (0001) hcp plane (3 bonds) makes it not possible to estimate the chemical component of the hcp Zr / bcc Nb interfacial energy using this simple nearest-neighbor bond approach. However, the above calculations for coherent bcc / bcc and hcp / hcp interfaces serve as a guide in assessing the order of magnitude of the chemical component of the interfacial energy for this system.

3.4.2 Coherency Biphase Boundary in Zr/Nb Multilayers

The experimental results indicated that the bcc coherency at the interface of Zr/Nb is established at a smaller layer thickness as compared with the initial bcc phase stability thickness. When a semi-coherent (assuming no strain in the multilayer) bcc \( \beta \)-Zr / bcc Nb multilayer transforms to a coherent bcc Zr / bcc Nb structure, there is no change in crystal structure. Thus, \( \Delta G = 0 \), and equating \( \Delta \gamma \)'s for coexisting phases (semi-coherent and coherent) yields,

\[
2 \Delta \gamma_{\text{semi}} = 2 \Delta \gamma_{\text{coh}} + Y m_0^2 \lambda \quad (3.14)
\]

Therefore Eq. (3.14) reduces to the equation of the coherent/semi-coherent biphase boundary given as
Note that $Y_{\text{bcc/bcc}}$ depends non-linearly on $f_{\text{Nb}}$, as expressed in Eq. (3.4). In order to estimate the value of $Y_{\text{bcc/bcc}}$, the elastic modulus of bcc Zr was taken from to be 90 GPa [19].

The difference between the structural interfacial energies of a semi-coherent bcc $\beta$-Zr / bcc Nb interface and a coherent bcc Zr / bcc Nb interface can again be estimated as the line energy (per unit area) of misfit dislocations at the semi-coherent $\{011\}$ bcc $\beta$-Zr // $\{011\}$ bcc Nb interface. This assumes that the coherency strains are completely relieved by misfit dislocations. Thus,

$$\gamma_{\text{bcc/bcc}}^{\text{coh}} - \gamma_{\text{bcc/bcc}}^{\text{inc}} = -\gamma_{\text{bcc/bcc}}^{\perp} = -140 \text{ mJ/m}^2$$

(3.16)

With the aid of Eq. (3.15), it was possible to calculate an approximate coherent/semi-coherent biphase boundary on the Nb/Zr diagram. This boundary is indicated by the dotted curve in Fig. 3.9. The points marked #2 (semi-coherent bcc b-Zr / bcc Nb) and #3 (coherent bcc Zr / bcc Nb) lie on either the dotted curve suggesting good agreement with experiment. But this curve falls above points marked #5 (semi-coherent bcc $\beta$-Zr / bcc Nb) and #6 (coherent bcc Zr / bcc Nb), indicating poor agreement at this different volume fraction of Nb. The dotted curve was drawn form Eq. (3.15) assuming the calculated $\Delta\gamma$ of $-140 \text{ mJ/m}^2$. By curve fitting this line such that it intersects between both sets of points labeled #2/#3 and #5/#6, an experimentally calculated interfacial energy of the bcc Nb / bcc Zr can be obtained. This is seen as the solid curve in Fig. 3.9. The value of $\Delta\gamma$ of the solid curve was $-160 \text{ mJ/m}^2$; this is in reasonable agreement with the O-lattice calculation used above.
Fig. 3.9 Coherency boundary between \( \text{bcc } \beta\)-Zr and coherent \( \text{bcc } \) Zr on the Zr/Nb biphasic diagram. The dotted curve is the predicted boundary and the solid curve is the experimentally determined boundary.
3.5 \textit{hcp} Nb in Zr/Nb Multilayers

The pseudomorphic \textit{bcc} phase of Zr is a direct consequence of the reduction in Zr/Nb interfacial energy accompanying the transformation from the bulk equilibrium \textit{hcp} Zr phase to the pseudomorphic \textit{bcc} Zr phase. The obvious question that arises is if a pseudomorphic \textit{bcc} form of Zr can be stabilized in relatively Nb-rich Zr/Nb multilayer, is it possible to stabilize a pseudomorphic \textit{hcp} Nb phase in relatively Zr-rich Zr/Nb multilayer? Unlike Zr, which undergoes an \textit{hcp} to \textit{bcc} allotropic transformation on its equilibrium phase diagram [1], no such allotropic transformation from \textit{bcc} to \textit{hcp} occurs for elemental Nb [1].

Using the classical thermodynamic framework of Eq. (3.1), a prediction for the phase stability region of \textit{hcp} Zr / \textit{hcp} Nb can be proposed. The slope that would separate the \textit{hcp} Zr / \textit{hcp} Nb and \textit{hcp} Zr / \textit{bcc} Nb biphase fields would be

\[ m_{\text{hcp/hcp}} = -\Delta G_{\text{Nb}}/2\Delta \gamma_{\text{hcp/hcp}} \]  

where \( \Delta G_{\text{Nb}} \) is the difference between the volumetric free energy of \textit{hcp} Nb and \textit{bcc} Nb and \( \Delta \gamma_{\text{hcp/hcp}} \) is the difference between the interfacial energy of a \textit{hcp} Zr / \textit{hcp} Nb interface and a \textit{hcp} Zr / \textit{bcc} Nb interface. Similar to the Zr pseudomorphic \textit{bcc} phase, \( \Delta G_{\text{Nb}} \) being a positive increase in energy would require a specific combination of \( \lambda \) and \( f_{\text{Nb}} \) such that the negative value of \( \Delta \gamma_{\text{hcp/hcp}} \) could dominate Eq. (3.1) and stabilize the \textit{hcp} Nb phase.

As a first approximation in predicting the \textit{hcp} Zr / \textit{hcp} Nb biphase stability field on the Zr/Nb biphase diagram, the value of \( \Delta \gamma_{\text{hcp/hcp}} \) was set equal to the experimentally determined value of \( \Delta \gamma_{\text{bcc/bcc}} \) in Eq. (3.8). Assuming that the atomic volume of \textit{hcp} Nb is similar to that of \textit{bcc} Nb, a solution thermodynamic calculation of \( \Delta G_{\text{Nb}} = 9.2 \times 10^8 \text{ J/m}^3 \) [8]
was coupled with $\Delta \gamma_{hcp/hcp}$ and Eq. (3.15) in predicting the slope of the $hcp \ Zr / hcp \ Nb - hcp \ Zr / bcc \ Nb$ boundary. The larger value of $\Delta G_{Nb}$ as compared to $\Delta G_{Zr} (= 3.7 \times 10^8 \ J/m^3)$ suggests that the $hcp \ Zr / hcp \ Nb$ stability region would be rather limited in extent as compared to the $bcc \ Zr / bcc \ Nb$ phase field. The predicted $hcp \ Zr / bcc \ Nb - hcp \ Zr / hcp \ Nb$ biphase boundary has been plotted as a dashed line in Fig. 3.10(a). Based on the classical thermodynamics framework of Eq. (3.1), the position and slope of the third biphase boundary, separating the $bcc \ Zr / bcc \ Nb$ and $hcp \ Zr / hcp \ Nb$ stability regions, is fixed once the other two boundaries are established. Since the slope of this third biphase boundary is inversely proportional to ($\Delta \gamma_{bcc/bcc} - \Delta \gamma_{hcp/hcp}$), in the first approximation, the slope will be infinite. In order to experimentally test the existence of the predicted region of $hcp \ Nb$ phase stability, a set of relatively Zr-rich Zr/Nb multilayers, corresponding to the points marked #9, #10, #11, and #12 on Fig. 3.10(b), have been sputtered deposited.

### 3.5.1 $hcp \ Nb$ Results

The transmission XRD pattern of the Zr/Nb #10 multilayer is shown in Fig. 3.11(a). The hexagonal $\{10\bar{1}0\}$ reflection is present but no $bcc \ Nb \ \{110\}$ reflection is observed. This is apparent by comparing this pattern with the transmission XRD pattern from the $hcp \ Zr / bcc \ Nb$ multilayer in Fig. 3.4(a). The location of the $\{110\}$ Nb reflection, with a FWHM peak position at $20.3^\circ \ 2\theta$, is evident in Fig. 3.4(a) but absent in Fig. 3.11(a). The absence of this peak for multilayer #10 indicates that the Nb layers have undergone a change in phase stability. In the transmission XRD pattern shown in Fig. 3.11(b), the $\{10\bar{1}0\} \ hcp$ and $\{10\bar{1}1\}$
Fig. 3.10 (a) Predicted hcp Zr / hcp Nb phase stability boundary on the Zr/Nb biphase diagram (b) Experimentally determined biphase stability boundary for hcp Zr / hcp Nb.
$hcp$ peaks are visible. The asymmetry of the $\{10\overline{1}0\}$ peak is clearly apparent in Fig. 3.11(c). This indicates that the multilayer has two distinct sets of $hcp$ lattice parameters. Pseudo-Voight deconvolution of the asymmetric $\{10\overline{1}0\}$ peak using MACDIFF software was used to calculate the $a$-lattice parameters for the two $hcp$ phases. The transmission XRD scan of Fig. 3.11(b) indicates a split in the $\{10\overline{1}1\}$ peak. Using the $a$-lattice parameters calculated from Fig. 3.11(c), the $c$-parameter for each of the $hcp$ phases was determined from the split in the $\{10\overline{1}1\}$ transmission XRD scan in Fig. 3.11(b). The transmission XRD $c$-lattice parameters were in good agreement with the $c$-parameters determined by the Pseudo-Voight deconvolution of the $\{0002\}$ intensity in the reflection XRD pattern from the same multilayer shown in Fig. 3.12. The lack of a significant split in the $\{0002\}$ peak in Fig. 3.12 for the two-$hcp$ phases is due to the substantially lower volume fraction of one phase, Nb, as compared to the other phase, Zr. Even so, a point of inflection is clearly visible in the slightly asymmetric $\{0002\}$ peak. The respective lattice parameters for each $hcp$ phase, as determined by XRD, in the as-deposited state are listed below:

$$a_1 = 3.15 \, \text{Å} ; c_1 = 5.12 \, \text{Å} \, \text{(Phase 1)}$$

$$a_2 = 3.21 \, \text{Å} ; c_2 = 5.10 \, \text{Å} \, \text{(Phase 2)}$$

In addition to the primary $\{0002\}$ peak, additional satellite peaks are visible in the reflection XRD pattern shown in Fig. 3.12. The presence and number of distinct satellite reflections in the RXRD pattern indicates that the film has maintained a layered structure. This was confirmed by a cross-section bright-field TEM micrograph, of this multilayer seen in Fig. 3.13.
Fig. 3.11(a) Transmission XRD pattern for Zr/Nb multilayer # 10. The pattern diffracts the $\{10\bar{1}0\}$ hcp peak but no $\{110\}$ bcc peak at $2\theta \approx 20.3^\circ$. (b) Transmission XRD pattern, with a slow scan rate, of the Zr/Nb multilayer #10 indicates the hcp diffracted intensities of $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$. (c) $\{10\bar{1}0\}$ peak is asymmetric.
Fig. 3.12 Reflection XRD pattern for Zr/NB multilayer #10. The \{0002\} has a point of inflection. Deconvolution has revealed two hcp phases contributing to this intensity.
Fig. 3.13 (a) Cross-section electron bright-field image of the Zr/Nb multilayer #10. The film exhibited a layered structure with morphologically sharp interfaces across the entire sample. (b) Cross-section electron bright-field image of the Zr/Nb multilayer #10 at a higher magnification.
In order to corroborate the XRD phase identification results, electron diffraction studies were conducted on plan-view TEM specimens of the same Zr/Nb #10 multilayer. A Selected Area Diffraction (SAD) pattern from this multilayer is shown in Fig. 3.14. This ring diffraction pattern can be consistently indexed based on two hcp phases, with the lattice parameters identical to those determined from the XRD studies listed previously. While the lattice parameters for phase 2 can be attributed to hcp Zr, the lattice parameters for the other hcp phase could not be attributed to any of the known equilibrium phases for Nb or Nb-Zr compounds or solid solutions. It is concluded that while the Zr layers retain its bulk equilibrium hcp structure, the Nb layers exhibits a novel hcp structure.

3.5.2 Discussion on hcp Nb Phase Stability

Recently G. Ghosh et al. [21] have used first principle calculations in determining the hcp Nb lattice parameters and have reported them to \( a = 2.8453 \) Å and \( c = 5.2551 \) Å. These values give a \( c/a \) ratio of 1.85 where as the experimentally determined \( c/a \) ratio for hcp Nb in this study is 1.625; a value very near the ideal \( c/a \) ratio of 1.63 for hcp materials [22]. The observation that the hcp Nb phase has adopted its own lattice parameters, or alternatively formed a semi-coherent interface with hcp Zr, suggests that the coherency strains are negligible and a linear boundary can be used in defining its phase field. This has been drawn as a solid line in Fig. 3.10(b).

Using the experimentally determined slope of the hcp Nb phase boundary in Fig. 3.10(b), the value of \( \Delta \gamma_{hcp/hcp} \) has been determined. The experimentally determined hcp Nb
**Fig. 3.14** Plan-view electron diffraction pattern of Zr/Nb multilayer #10. The pattern is consistently indexed as two hcp phases with lattice values consistent with the transmission XRD results of Fig. 3.11.
lattice values were used to refine the atomic volume average used in the calculation of the volumetric free energy difference (ΔG_{Nb}). The refined ΔG_{Nb} value is 8.3x10^8 J/m³. Coupling this value and the slope, 0.86 nm⁻¹, to Eq. (3.17), \( \Delta \gamma_{\text{hcp/hcp}} \approx -480 \text{mJ/m}² \). The lattice parameters and densities of the various phases in Zr/Nb are listed in Table 3.2 with the corresponding transformation energies for Zr/Nb in Table 3.3.

### 3.6 Summary of Zr/Nb Phase Stability

Based on a classical thermodynamic model of phase stability in multilayered materials, the phase stability of bcc Zr in Zr/Nb multilayers has been investigated in detail. Using a previously reported experimental result for the phase stability of bcc Zr in these multilayers, coupled with a thermodynamics model, a biphase diagram has been proposed. A series of Nb-rich volume fraction Zr/Nb multilayers with varying bilayer thicknesses on either side of the predicted biphase boundary have been sputter deposited. Transmission XRD and plan-view electron diffraction patterns are in agreement with the predictions afforded by the proposed biphase diagram. From the experimentally determined slope of the hcp Zr / bcc Nb - bcc Zr / bcc Nb biphase boundary, the reduction in the interfacial energy accompanying the change in phase stability from hcp to bcc Zr has been estimated, \( \Delta \gamma_{\text{bcc/bcc}} = -250 \text{ mJ/m}² \).

First approximation calculations were used to assess the structural and chemical contributions to the interfacial energy. The O-lattice generated dislocation network suggests that the structural component of the interfacial free energy is large enough to drive the
<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice Parameter</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc Nb</td>
<td>(a = 3.30 , \text{Å})</td>
<td>8.6 g/cc</td>
</tr>
<tr>
<td>hcp Zr</td>
<td>(a = 3.21 , \text{Å}; , c = 5.10 , \text{Å})</td>
<td>6.7 g/cc</td>
</tr>
<tr>
<td>bcc (\beta)-Zr</td>
<td>(a = 3.54 , \text{Å})</td>
<td>6.8 g/cc</td>
</tr>
<tr>
<td>hcp Nb</td>
<td>(a = 3.15 , \text{Å}; , c = 5.12 , \text{Å})</td>
<td>7.0 g/cc</td>
</tr>
<tr>
<td>coherent bcc</td>
<td>(a = 3.38 , \text{Å})</td>
<td>7.8 g/cc, 8.0 g/cc</td>
</tr>
</tbody>
</table>

**Table 3.2** Crystallographic properties of various phases stabilized in Zr/Nb multilayers

<table>
<thead>
<tr>
<th>(\Delta G) free energy</th>
<th>Zr (J/m(^3))</th>
<th>Nb (J/m(^3))</th>
<th>bcc/bcc (mJ/m(^2)) measured</th>
<th>hcp/hcp (mJ/m(^2)) measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G)</td>
<td>(3.7 \times 10^8)</td>
<td>(8.3 \times 10^8)</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>(\Delta \gamma)</td>
<td>----</td>
<td>----</td>
<td>-250</td>
<td>-480</td>
</tr>
</tbody>
</table>

**Table 3.3** Energies of Zr/Nb multilayers
change in phase stability. Furthermore, for a fixed volume fraction of Nb, the phase stability path of $hcp$ to $bcc$ Zr has been found to be semi-coherent $bcc$ $\beta$-Zr, then coherent $bcc$ Zr to the $bcc$ Nb interface with decreasing bilayer spacing $\lambda$. Coupling the simple thermodynamics of the proposed model with linear elasticity theory, a coherency boundary between semi-coherent $bcc$ $\beta$-Zr / $bcc$ Nb and coherent $bcc$ Zr / $bcc$ Nb has been calculated. Reasonable agreement was found between calculated and experimentally determined values for the interfacial energies associated with these phase stability regions.

Similar to the pseudomorphic $bcc$ Zr predictions, the thermodynamic model has been used to predict and subsequently confirm a region of novel $hcp$ Nb phase stability. The formation of this novel phase has been systematically predicted and experimentally confirmed rather than being serendipitously discovered. The $hcp$ Nb phase has adopted its own lattice parameters that are different from those of $hcp$ Zr. Based on these observations, a complete Zr/Nb phase stability diagram has been constructed that can be used as a tool to predict which combinations of volume fractions and length scales can stabilize pseudomorphic phases in this system.
References for Chapter 3

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PSEUDOMORPHIC PHASE STABILITY AND PHASE ENGINEERING
IN TITANIUM / NIOBIUM MULTILAYERS

4.1 Ti/Nb Multilayers

The successful application of the classical thermodynamic biphase stability diagram has been demonstrated with the Zr/Nb multilayers of Chapter 3. Similar to Zr, Ti undergoes an allotropic \textit{hcp} $\alpha$ to \textit{bcc} $\beta$ phase transformation at 1173 K and 1 atm [1]. Since each of these metals share similar physical properties, \textit{hcp} to \textit{bcc} phase stability should also be exhibited in Ti/Nb multilayers. Zheng \textit{et al.} [2], while investigating the superconducting properties of Ti/Nb multilayers, have reported phase stability changes in the Ti layer. Unfortunately, details of layer thickness and volume fractions for changes in phase stability were not listed in their work.

As previously done for the Zr/Nb system, the thermodynamic framework for Ti/Nb phase stability is given as [3]

$$\Delta g = 2\Delta \gamma + [\Delta G_{\text{Nb}} f_{\text{Nb}} + \Delta G_{\text{Zr}} (1-f_{\text{Nb}})] \lambda$$

(4.1)
where $\Delta g$ is the total free energy change per unit of interfacial area, $\Delta \gamma$ is the interfacial free energy reduction between the pseudomorphic and equilibrium states, $\Delta G_i$ is the allotropic volumetric free energy difference between the pseudomorphic and bulk equilibrium states of layer $i$, $\lambda$ is the bilayer thickness, and $f_{Nb}$ is the volume fraction of Nb.

### 4.2 Predicting bcc Ti Phase Stability

To establish the hcp Ti / bcc Nb – bcc Ti / bcc Nb phase stability fields, a biphase linear boundary, assuming negligible coherency strains, with the slope of

$$\text{slope} = \frac{\Delta G_{Ti}}{2\Delta \gamma_{bcc/bcc}}$$

is plotted in Fig. 4.1(a). The $\Delta G_{Ti}$ value was taken from CALPHAD calculations [16] using an atomic volume average of hcp Ti and bcc Ti as done previously with Zr/Nb multilayers of Chapter 3. As a first approximation for the interfacial energy reduction, the $\Delta \gamma_{bcc/bcc}$ was taken to equal –250 mJ/m$^2$; the experimentally determined interfacial free energy reduction for hcp Zr to bcc Zr in Zr/Nb multilayers. Unlike the predicted hcp to bcc Zr boundary in Zr/Nb, no such data points exist for Ti/Nb. As established in Chapter 1 and shown in Chapter 3, the thermodynamics of this boundary requires the slope to approach $\lambda \cdot 1 = 0$ as $f_{Nb} = 1$.

Using the predicted boundary in Fig. 4.1(a) as an experimental guide, a series of Ti/Nb multilayers have been sputtered deposited and are tabulated in Table 4.1 and plotted in Fig. 4.1(b). Figs. 4.2(a) and 4.2(b) are representative TEM plan-view and cross-section bright-field images of the Ti/Nb multilayers deposited in this study. Similar to Zr/Nb, the films are polycrystalline with grain sizes of 15 nm - 50 nm.
Fig. 4.1 (a) Predicted hcp to bcc phase stability boundary for Ti in Ti/Nb multilayers (b) Deposited Ti/Nb multilayers based upon the predicted boundary. The solid line represents the experimentally determined boundary for Ti phase stability. Comparison to (a) indicates that it is significantly lower than the original prediction.
<table>
<thead>
<tr>
<th>#</th>
<th>Phase (Ti/Nb)</th>
<th>(\lambda) (nm)</th>
<th>(f) Nb</th>
<th>EDS Nb (at.%)</th>
<th>Sputt.Pwr (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>hcp/bcc</td>
<td>14.0</td>
<td>0.82</td>
<td>87</td>
<td>100</td>
</tr>
<tr>
<td>#2</td>
<td>bcc/bcc</td>
<td>9.9</td>
<td>0.72</td>
<td>83</td>
<td>100</td>
</tr>
<tr>
<td>#3</td>
<td>bcc/bcc</td>
<td>6.3</td>
<td>0.71</td>
<td>83</td>
<td>100</td>
</tr>
<tr>
<td>#4</td>
<td>bcc/bcc</td>
<td>4.3</td>
<td>0.70</td>
<td>81</td>
<td>100</td>
</tr>
<tr>
<td>#5</td>
<td>hcp/bcc</td>
<td>7.5</td>
<td>0.51</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>#6</td>
<td>bcc/bcc</td>
<td>5.6</td>
<td>0.45</td>
<td>62</td>
<td>100</td>
</tr>
<tr>
<td>#7</td>
<td>bcc/bcc</td>
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<td>0.44</td>
<td>59</td>
<td>100</td>
</tr>
<tr>
<td>#8</td>
<td>bcc/bcc</td>
<td>4.0</td>
<td>0.43</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>#9</td>
<td>bcc/bcc</td>
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<td>0.40</td>
<td>55</td>
<td>100</td>
</tr>
<tr>
<td>#10</td>
<td>hcp/bcc</td>
<td>6.8</td>
<td>0.46</td>
<td>55</td>
<td>100</td>
</tr>
<tr>
<td>#11</td>
<td>hcp/bcc</td>
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<td>0.32</td>
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<td>100</td>
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<tr>
<td>#12</td>
<td>hcp/bcc</td>
<td>26.9</td>
<td>0.16</td>
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<td>100</td>
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<tr>
<td>#13</td>
<td>hcp/hcp</td>
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<td>100</td>
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<tr>
<td>#14</td>
<td>hcp/hcp</td>
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<td>0.12</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
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<td>0.15</td>
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<tr>
<td>#16</td>
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<td>100</td>
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<tr>
<td>#17</td>
<td>hcp/hcp</td>
<td>1.91</td>
<td>0.12</td>
<td>15</td>
<td>100</td>
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**Table 4.1** Deposited Ti/Nb multilayers
Fig. 4.2 (a) Plan-view electron bright-field image of a representative Ti/Nb multilayer (b) Cross-section electron bright-field image of a representative Ti/Nb multilayer. The films exhibit uniform lamellar interfaces consistent with the other multilayers deposited in Chapter 3.
4.2.1 $bcc$ Ti Results

As can be seen in Fig. 4.1(b), the Ti layers transformed to $bcc$ Ti, but at a bilayer thickness much larger than predicted. This could be expected since the interfacial energy reduction term, used in Eq. (4.2), was for Zr/Nb. Obviously, Zr and Ti having different lattice parameters would contribute a different structural component to the interfacial free energy as well as a different chemical contribution to the bonding. But the predicted boundary provided an initial experimental starting point for investigating the location of $bcc$ Ti phase stability in Ti/Nb.

The phase stability change was confirmed by XRD and electron diffraction. As can be seen in the reflection XRD plot in Fig. 4.3(a) for multilayer #5 in Fig. 4.1(b), both the $hcp$ Ti and $bcc$ Nb peaks are present. Each film exhibited a preferred growth texture in its closest packed planes. The bulk equilibrium phase structure of the Ti/Nb multilayer #5 was confirmed by plan-view TEM electron diffraction in Fig. 4.3(b). The presence of satellite peaks in Fig. 4.3(a) confirms that the multilayer has a chemically modulated structure. Upon a reduction in thickness for a fixed volume fraction, Ti/Nb multilayer #6 under went a change in phase stability from $hcp$ Ti to $bcc$ Ti. As evident in the reflection XRD pattern of Fig. 4.4(a), the $\{0002\}$ $hcp$ peak is no longer present; only a single $\{011\}$ $bcc$ peak is diffracting. The $bcc$ Ti phase stability was additionally confirmed by plan-view electron diffraction in Fig. 4.4(b). Further confirmation of the phase stability change can be seen in the transmission XRD pattern of Fig. 4.4(c). The $\{10\overline{1}0\}$ $hcp$ Ti peak’s location is marked in Fig. 4.4(c) and is clearly absent in the transmission XRD pattern. The other multilayers
Fig. 4.3 (a) Reflection XRD pattern for Ti/Nb multilayer #5. The hcp Ti (0002) and bcc Nb (011) textured peaks are present (b) Plan-view electron diffraction pattern for Ti/Nb multilayer #5 which is consistently indexed as hcp Ti and bcc Nb.
Fig. 4.4 (a) Reflection XRD pattern for Ti/Nb multilayer #6. A single bcc (011) peak is present for both Ti and Nb (b) Plan-view electron diffraction pattern for Ti/Nb multilayer #6 which is consistently indexed as a coherent bcc / bcc structure (c) Transmission XRD pattern for the Ti/Nb multilayer #6 diffracting a single (110) bcc intensity.
listed in Fig. 4.1(b) and tabulated in Table 4.1 have been confirmed by similar characterization methods.

The Ti/Nb multilayers’, like the Zr/Nb multilayers’, XRD and plan-view electron diffraction data indicated that the $hcp/bcc$ interface was Burgers or near Burgers given as

$$\{0001\}_{hcp} // \{011\}_{bcc}$$

$$<1120>_{hcp} // <111>_{bcc}$$

Upon transformation to a $bcc/bcc$ interface, the orientation relationship for Ti/Nb was identical to Zr/Nb and is given as

$$\{011\}_{bcc} // \{011\}_{bcc}$$

$$<111>_{bcc} // <111>_{bcc}$$

### 4.2.2 Discussion on $bcc$ Ti Phase Stability

Similar to Zr’s phase stability change from $hcp$ to $bcc$, Ti has experienced a $hcp$ to $bcc$ phase transformation in a similar region of Nb-rich volume fraction multilayers. Upon initial change in phase stability, the $bcc$ Ti layer has adopted its $\beta$-Ti lattice parameter. $\beta$-Ti’s lattice parameter extrapolated to room temperature, is 3.28 Å; a value nearly equivalent to Nb’s $bcc$ lattice parameter of 3.30 Å. Even though the $bcc$ Ti / $bcc$ Nb interface is coherent, the coherency strains are negligible due to the similar lattice parameters and the $hcp$ Ti / $bcc$ Nb - $bcc$ Ti / $bcc$ Nb boundary, referenced to the experimentally determined data points, can be drawn linearly in Fig. 4.1(b).
Using the slope of the bcc/bcc boundary coupled to a solution-based $\Delta G_{Ti}$ value [16], the interfacial free energy reduction, $\Delta \gamma_{bcc/bcc}$, was calculated from Eq. (4.2) to be approximately $-580$ mJ/m$^2$. The energetic terms for Ti/Nb multilayers are listed in Table 4.2. The $\Delta G_{Ti}$ from literature was converted from J/mol to J/m$^3$ using an average atomic volume of hcp and bcc Ti. The interfacial free energy reduction is nearly twice the value for hcp Zr to bcc Zr phase change in Zr/Nb multilayers. This is reflected in the substantially larger critical transformation layer thickness for a similar volume fraction of Nb. Fig. 4.5 is a plot comparing the hcp / bcc – bcc / bcc boundaries for these two systems. The solid line is the biphase boundary for the Zr/Nb multilayers whereas the dotted line is the biphase boundary for the Ti/Nb multilayers. Recall that the y-axis is the inverse of the bilayer thickness; therefore, a larger layer thickness is lower on the y-axis scale. Initially this can be quite surprising if one considers the misfit reduction between the Zr/Nb and Ti/Nb multilayers accompanying the hcp to bcc transformation.

Using the A/B orientation relationships given above and the lattice parameters shown in Tables 3.3 and 4.1, the misfit for the hcp/bcc and bcc/bcc interfaces was determined along the best-fit direction, i.e. the $<1\bar{1}20>$/<$111>$ and $<111>/<$111>$ respectively. The Zr/Nb interface misfit is reduced from 12% to 7% upon the change from hcp Zr to $\beta$-Zr. Ti/Nb exhibits a reduction from 3% to $\approx 0\%$ for the hcp Ti to $\beta$-Ti interface. The relative misfit reduction from a hcp/bcc to a bcc/bcc interface is slightly greater for Zr/Nb than for Ti/Nb.

A van der Merwe interface model [5-6] for two semi-infinite overgrowths has been used to estimate the change in interfacial free energy as a function of misfit. This simple model considers the total interfacial free energy, $E$, between two semi-infinite overgrowths.
<table>
<thead>
<tr>
<th>$\Delta_{\text{free energy}}$</th>
<th>Ti (J/m$^3$)</th>
<th>Nb (J/m$^3$)</th>
<th>$\text{Ti}_8\text{V}$ (J/m$^3$)</th>
<th>$\text{bcc/bcc}$ (mJ/m$^2$) measured</th>
<th>$\text{hcp/hcp}_2$ (mJ/m$^2$) measured</th>
<th>$\text{bcc/bcc}_{\text{Ti-15Nb}}$ (mJ/m$^2$) predicted</th>
<th>$\text{bcc/bcc}_{\text{Ti-15Nb}}$ (mJ/m$^2$) predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G$</td>
<td>$3.5 \times 10^8$</td>
<td>$8.3 \times 10^8$</td>
<td>$2.5 \times 10^8$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$\Delta \gamma$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>-580</td>
<td>-850</td>
<td>-265</td>
<td>-280</td>
</tr>
</tbody>
</table>

**Table 4.2** Energies of Ti/Nb multilayers
**Fig. 4.5** Comparison the *hcp-bcc* phase stability boundary for Zr and Ti in Zr/Nb and Ti/Nb multilayers.
in contact at a single interface. The total interfacial energy is given as a linear combination of the potential energy, $E_p$, and the strain energy, $E_s$, at the interface by the following:

$$E = E_p + E_s = (\mu F^2/4\pi d)(1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln[2 \beta (1 + \beta^2)^{1/2} - 2 \beta^3])$$  \hspace{1cm} (4.3)

where $\mu_i$ is the interfacial shear modulus (taken to be the average of the two constituent phases), $c$ is a spacing parameter formed by the superposition of the two lattices in contact at the interface, $d$ is the distance between the two atomic planes on either side of the interface, and $\beta$ is a function that contains all the significant contributions to the interfacial energy such as misfit and the elastic constants of the crystals. $\beta$ is given as

$$\beta = 2\pi d \lambda / \mu_i p$$  \hspace{1cm} (4.4)

where the terms $d$ and $\mu_i$ are defined above, and $p$ is the measure of misfit

$$p = (a-b)/[1/2(a+b)]$$  \hspace{1cm} (4.5)

where $a$ and $b$ are the respective crystallographic lattice parameters determined by the orientation relationship. Finally $\lambda$, from Eq. (4.4), is defined as

$$\lambda = [(1-\nu_\lambda)/\mu_\lambda] + [(1-\nu_\nu)/\mu_\mu]^{-1}$$  \hspace{1cm} (4.6)

where $\nu_i$ is Poisson’s ratio of layer $i$ and $\mu_i$ is the shear modulus of layer $i$. The elastic constants used in the calculations are given in Table 4.3.

Figs. 4.6(a) and 4.6(b) are the calculated plots of the change in interfacial energy as a function of $\beta$ for the hcp/bcc and bcc/bcc interfaces in Zr/Nb and Ti/Nb systems. The arrows mark the experimentally determined value of $\beta$ for each multilayer in its respective phase stability condition and misfit at the interface. The difference in the interfacial energy value for each $\beta$ is the total reduction in interfacial energy upon phase transformation. These plots exhibit how interfacial energy scales with $\beta$. As $\beta$, which is a measure of the misfit,
### Table 4.3 Elastic constants used in van der Merwe interfacial energy model

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\nu$</th>
<th>$\mu$ (GPa)</th>
<th>[ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$hcp , \alpha$-Zr</td>
<td>0.38</td>
<td>35</td>
<td>8</td>
</tr>
<tr>
<td>$hcp , \alpha$-Ti</td>
<td>0.361</td>
<td>45.6</td>
<td>8</td>
</tr>
<tr>
<td>$bcc , \beta$-Zr</td>
<td>0.39</td>
<td>27.1</td>
<td>22</td>
</tr>
<tr>
<td>$bcc , \beta$-Ti</td>
<td>0.372</td>
<td>33</td>
<td>22</td>
</tr>
<tr>
<td>$bcc , Nb$</td>
<td>0.397</td>
<td>37.5</td>
<td>8</td>
</tr>
</tbody>
</table>
Fig. 4.6 (a) Interfacial energy verses a representation of misfit for hcp Zr / bcc Nb and bcc β-Zr / bcc Nb. The experimental value of β is marked on the curves by an arrow (b) Interfacial energy verses a representation of misfit for hcp Ti / bcc Nb and bcc β-Ti / bcc Nb. The experimental value of β is marked on the curves by an arrow.
increases, the interfacial energy also increases. The greatest increase in interfacial energy occurs with the initial insertion of misfit dislocations (low $\beta$ values). This trend explains why Ti has a greater driving force for the hcp-bcc transformation. When Ti undergoes a phase stability change from hcp to bcc, it is able to significantly reduce its interfacial energy by the formation of a coherent interface or, alternatively, the strain energy component of the interfacial energy rapidly approaches zero. Though Zr has a greater overall reduction in misfit upon a change in phase stability, it is unable to reduce the strain component of the interfacial energy to zero because it has formed a semi-coherent interface with Nb.

The calculated interfacial free energy difference, using this model, for the Ti/Nb multilayer is approximately $-280 \text{ mJ/m}^2$ as compared to Zr/Nb’s interfacial free energy difference of $-240 \text{ mJ/m}^2$. These values follow the trend of the $\Delta \gamma_{\text{bcc/bcc}}$’s in Table 3.3 and 4.2 that Ti/Nb has a greater reduction in the interfacial energy. Interestingly, the predicted interfacial energy change of Zr/Nb by the van der Merwe model is very similar to the experimentally determined value of $-250 \text{ mJ/m}^2$. The Ti/Nb multilayer’s $\Delta \gamma_{\text{bcc/bcc}}$ experimental value was higher than this prediction. This will be addressed in more detail in Section 4.4 but, in general, the discrepancies of the calculated values to the experimentally determined values can be due to the simplicity of the van der Merwe model and the assumptions associated with the model. The model assumes a single interface where multilayers have numerous interfaces. The elastic constant values used in these calculations are those which correspond to classical length scales and may not be accurate at the nanometer length scales involved in these multilayers. Despite these assumptions, it is encouraging to note that this simple model, based on classical approximations, was able to give reasonable interfacial
energy differences that are in the correct order of magnitude and also predict realistic trends. These calculations have provided additional insight into explaining why the Ti layers in Ti/Nb multilayers exhibit a substantially greater critical \textit{hcp-bcc} transformation thickness as compared with the Zr layers in Zr/Nb multilayers.

4.3 \textit{hcp Nb in Ti/Nb Multilayers}

The thermodynamic framework of Eq. (4.1) has been successfully used to predict and model \textit{hcp} to \textit{bcc} phase stability in Ti for Ti/Nb multilayers. Extending the same thermodynamic framework with the successful prediction of \textit{hcp} Nb in Zr/Nb, a similar \textit{hcp} Nb phase field should exist in Ti-rich volume fraction Ti/Nb multilayers. The prediction of this boundary was done in a similar manner as in Chapter 3’s Section 3.5. The slope of the boundary separating the \textit{hcp Ti} / \textit{bcc Nb} – \textit{hcp Ti} / \textit{hcp Nb} phase fields, assuming negligible coherency strains, is

\[ \text{slope} = -\frac{\Delta G_{Nb}}{2\Delta \gamma_{hcp/hcp}} \]  

\[ (4.7) \]

where $\Delta G_{Nb}$ is the volumetric free energy change from \textit{hcp} to \textit{bcc} Nb and whose value is taken from Chapter 3’s Section 3.5.2 to equal $8.3 \times 10^8$ J/m$^3$. Similarly, $\Delta \gamma_{hcp/hcp}$ is the reduction in interfacial free energy accompanying the phase transition and will be assumed to equal –580 mJ/m$^2$, the experimentally determined $\Delta \gamma_{bcc/bcc}$ value for Ti/Nb. A predicted \textit{hcp/hcp} boundary was drawn in Fig. 4.7(a). Based upon this predicted \textit{hcp/hcp} phase field, a series of Ti-rich multilayers have been sputtered deposited in this region. These multilayers have been listed in Table 4.1 and plotted in Fig. 4.7(b).
Fig. 4.7 (a) Predicted \textit{hcp} Nb phase stability field in Ti/Nb. (b) Series of Ti/Nb multilayers deposited in the Ti-rich region of (a) were grown to determine the \textit{hcp} Nb phase stability boundary. The experimentally determined \textit{hcp} Nb phase boundary has been marked as a solid line.
4.3.1 Results of $hcp$ Nb

Fig. 4.8(a) is the plan-view electron diffraction pattern for the Ti/Nb multilayer #14. The pattern was consistently indexed based upon $hcp$ Ti / $hcp$ Nb. The $hcp$ Nb phase, like $hcp$ Nb in Zr/Nb multilayers, has clearly adopted its own lattice parameters and whose lattice parameters, within the ~ 5% error of this measurement technique, are identical to $hcp$ Nb in Zr/Nb. The (1010) $hcp$ Nb ring is clearly separate and distinct from all of the other rings in this pattern. The $a$-lattice parameter as well as the $c$-lattice parameter were determined by the {1010} and {1011} rings. The $hcp$ lattice parameters have been listed in Table 4.4.

Fig. 4.8(b) is the reflection XRD pattern for multilayer #14. The {011} peak, which has been resolved as a split from {0002} in previous XRD patterns (Fig. 4.3(a)) is not present. This is additional confirmation of the phase stability change from $bcc$ Nb to $hcp$ Nb indexed in the plan-view electron diffraction pattern of Fig. 4.8(a). Unfortunately, the {0002} peak of $hcp$ Nb overlaps a satellite intensity generated by diffraction from the layered structure of the multilayer. The presence of the satellite intensities in Fig. 4.8(b) indicates a chemically modulated structure that has been verified by the cross-section electron bright-field image in Fig. 4.9(a). The cross-section electron diffraction pattern for Ti/Nb multilayer #14 in Fig. 4.9(b) was indexed based upon the two $hcp$ structures with the lattice parameters listed in Table 4.4. Again, the satellite intensity from the chemically modulated structure of the multilayer has overlapped the {0002} peak of $hcp$ Nb. The presence of $hcp$ Ti, and not $fcc$
Fig. 4.8 (a) Plan-view electron diffraction pattern from Ti/Nb multilayer #14. The pattern has been consistently indexed as two hcp phases. The hcp Nb lattice values were the same as the hcp Nb phase stabilized in Zr/Nb. (b) Reflection XRD pattern for Ti/Nb multilayer #14. The (0002) Ti peak is not split, indicative of the absence of bcc Nb (011). hcp Nb’s (0002) peak is overlapped with the $n=+1$ satellite reflection from the chemical modulated structure of the multilayer.
Fig. 4.9 (a) Cross-section electron bright-field image of *hcp* Ti / *hcp* Nb multilayer #14. The multilayer has clearly maintained a layered morphology. (b) Cross-section electron diffraction pattern of the *hcp* Ti / *hcp* Nb multilayer. The presence of *hcp* Ti, and not *fcc* Ti, indicates that the type of interface is a significant factor in contributing to the formation of *fcc* stabilized δ-TiH$_2$ discussed in section 2.4.3.
Ti as discussed in Chapter 2 Section 2.4.3, demonstrates that a Ti surface alone is not sufficient to facilitate hydrogen stabilized $fcc \delta$-TiH$_2$ in the cross-section. The presence of $fcc$ interfaces for Ti/$fcc$ metal multilayers must also be a significant factor in contributing to $hcp$ Ti to $fcc$ $\delta$-TiH$_2$ stabilization in the cross-section.

4.3.2 Discussion of $hcp$ Nb Phase Stability

The $hcp$ Nb phase, like $hcp$ Nb in Zr/Nb multilayers, has clearly adopted its own lattice parameter. This indicates that the transformation is not dictated by coherency strains at the interface and a linear boundary can be drawn between the $bcc$ Nb and $hcp$ Nb phase fields on the biphase diagram of Fig. 4.1(b). The negligible coherency strains and the similarity of the $hcp$ lattice parameters between the two $hcp$ Nb phases in Zr/Nb and Ti/Nb suggests that these are Nb’s equilibrium $hcp$ lattice parameters. Using the slope of the $hcp$ Ti / $hcp$ Nb – $hcp$ Ti / $bcc$ Nb boundary and Eq. (4.7), the interfacial free energy reduction for this change in phase stability is $\approx -850 \text{ mJ/m}^2$. The fairly large $\Delta\gamma_{hcp/hcp}$ is surprising but still within the order of magnitude of solid-solid interfacial energies [7]. The lattice parameters and density for the various phases stabilized in Ti/Nb is listed in Table 4.4.

4.4 Atom Probe Tomography

3D Atom Probe (3DAP) Tomography is a characterization technique that has been used to establish the atomic arrangement of the chemical profile for the Ti/Nb multilayers. Developing the chemical profile for these multilayers is extremely relevant in understanding
### Table 4.4

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice Parameters</th>
<th>density</th>
</tr>
</thead>
<tbody>
<tr>
<td>$hcp$ $\alpha$-Ti</td>
<td>$a = 2.95 , \text{Å}$ $c = 4.68 , \text{Å}$</td>
<td>4.5 g/cc</td>
</tr>
<tr>
<td>$bcc$ $\beta$-Ti</td>
<td>$a = 3.30 , \text{Å}$</td>
<td>4.4 g/cc</td>
</tr>
<tr>
<td>$bcc$ Nb</td>
<td>$a = 3.30 , \text{Å}$</td>
<td>8.6 g/cc</td>
</tr>
<tr>
<td>$hcp$ Nb</td>
<td>$a = 3.15 , \text{Å}$ $c = 5.10 , \text{Å}$</td>
<td>7.0 g/cc</td>
</tr>
</tbody>
</table>

Table 4.4 Lattice parameters and corresponding density for phases stabilized in Ti/Nb.
the atomic interaction each individual layer may have on the phase stability of the other layer. Nb, being a β-stabilizer for Ti, could help to facilitate the bcc phase stability of Ti by intermixing at the interface.

4.4.1 Atom Probe Results

Figs. 4.10(a) and 4.10(b) are the reflection XRD pattern and the plan-view electron diffraction pattern respectively for the Ti/Nb multilayer that was prepared for 3DAP. The patterns were indexed as a bcc Ti / bcc Nb structure. No clear split in the \{0002\} Ti and \{011\} Nb peak from the XRD pattern exists. It does exhibit a ‘flat-top’ at the maximum of the intensity peak. The electron diffraction pattern did not diffract any distinguishable and separate hcp rings in the plan-view diffraction pattern. A smeared intensity from the \{10\bar{1}0\} diffraction intensity location to the distinct (110) ring is present in Fig. 4.10(b). These diffraction patterns indicate that this multilayer is at or very near the critical transition thickness. Its bilayer spacing of 4.75 nm and $f_{\text{Nb}} = 40\%$ would place it on the phase stability boundary of the Ti/Nb biphase diagram.

Once the specimen was prepared as an atom probe tip, as described in Chapter 2 Section 2.5.1, it was loaded into the chamber and a specific region near the apex of the tip was selected and field evaporated. Fig. 4.11(a) is the spectrum of the ions collected to the mass-to-charge ratio. The $H_2^+$, Ti$^{2+}$, Nb$^{3+}$, and Nb$^{3+}$ peaks have all been labeled in Fig. 4.12(a).
**Fig. 4.10** (a) Reflection XRD pattern of the Ti/Nb multilayer prepared for atom probe analysis. The pattern has been indexed as a bcc Ti / bcc Nb structure. (b) Plan-view electron diffraction pattern of the Ti/Nb multilayer prepared for atom probe analysis. The pattern did not diffract any distinguishable hcp rings, but clearly a spread in the \{110\} intensity exists indicating that the sample is at or near the critical transition layer for hcp to bcc Ti phase stability.
Fig. 4.11 (a) Mass-to-charge spectrum of collected atoms from the analyzed region of the Ti/Nb multilayer. (b) Reconstructed atom probe image of the selected area of the Ti/Nb multilayer that was field evaporated and collected. The layers clearly indicate a change in thickness with elapsed collection time. This artifact is a result of field evaporation at the standing voltage. With elapsed time, the artifact is diminished. (c) Reconstructed atom probe images of H$_2$, Ti, and Nb in the layered multilayer. Note the affinity of Ti with hydrogen.
The collected field evaporated atoms of this region have been reconstructed and can be seen in Fig. 4.11(b). Each dot represents an individual atom. The edges of the reconstructed region have fluctuated due to the different field evaporation rates of Ti and Nb. The individual layering of the multilayer has also been shown to increase with distance into the reconstructed image. This layering change is due to a rather unique problem associated with atom collection from these specimens (discussed below).

The presence of hydrogen is a result of specimen preparation during the milling process. As discussed in Chapter 2 Section 2.4.3, a freshly milled surface that does not have a diffusion barrier layer can not prevent interdiffusion of hydrogen into the multilayer stack. As seen in Fig. 2.14, the atom probe tip is milled in such a geometry that the entire stack of layers are exposed to atmosphere. This allows hydrogen to be infiltrated into the Ti layers. Fig. 4.11(c) is the reconstructed image of hydrogen atoms to Ti atoms position in the stack. It is clear that Ti has an affinity for hydrogen. The lack of $fcc \delta$-TiH$_2$ in the previous diffraction patterns of the multilayers, as well as the partial pressure background gases within the deposition chamber (Section 2.1.3) clearly indicate that this hydrogen contamination did not result during the growth but rather ion milling in the DB-235 FIB instrument.

The pronounced mass tails from the evaporated multilayer’s ions in the spectra of Fig. 4.11(a) is atypical of many metallic specimens [11]. The tails degrade the mass resolution of the spectra and complicate the estimation of the concentrations due to peak overlap. These tails are indicative of poor conduction [11]. Poor conduction reduces the amplitude of the high voltage pulse used to initiate the field evaporation. This causes a deficiency in field evaporated ions. The change in layering is caused by uncontrolled evaporation of the
ions at the standing voltage. These uncontrolled ions are then contributed to the noise background [11]. Since the timing system for the collection of ions is only active 0.6% of the time, approximately 166 times more ions are lost for each noise event. As uncontrolled field evaporation is reduced, the effective capture of ions increases and manifests itself as a thicker layer with time.

The uncontrolled field evaporation may be a result of the temperature at the analysis surface of the multilayers becoming stable with elapsed time of the experiment. The change in temperature is could be due to the poor electrical and thermal connection of the stainless steel biological needle used for mounting the Si post. Alternatively, the high resistance of the Si post could be a contributing factor. Future specimens should be prepared on heavily doped Si wafers to increase the electrical conductivity. A recommended resistivity for the Si wafer post should be less then 0.05 Ω-cm [24]. The uncontrolled field evaporation was more prevalent in the Ti layers then the Nb layers due to its lower evaporation field.

To reduce the influence of the changing layer thickness, only a section of 7.4 nm x 17 nm x 32.7 nm near center and base of the reconstructed region was used in the analysis. This smaller section’s location in the specimen was significantly far from the field evaporation artifacts near the edges as well as the transit uncontrolled evaporation near the tip.

The reconstructed Ti and Nb atoms for this region are shown in Fig. 4.12(a). As can be seen in this figure, the thickness for the individual layers are nearly constant. The bilayer spacing, determined by the satellite peak spacing in the reflection XRD pattern of Fig. 4.10(a), matched well to the reconstructed bilayer thickness. This indicates that the changing layer thickness artifacts are minimal in this region. As compared to the Ti layers (lighter
Fig. 4.12 (a) Reconstructed atom probe region used in the analysis. The Nb atoms (darker shade or red) have significantly interdiffused into the Ti layers (lighter shade or green). (b) Composition profile of the reconstructed Ti/Nb multilayer in (a).
Fig. 4.13 (a) Compositional contour map of Fig. 4.13(a) at 16% Nb (b) Compositional contour map of Fig. 4.13(a) at 9% Ti.
shade or green), the Nb atoms (darker shade or red) appear to have sufficiently interdiffused into the Ti layers. A compositional profile, Fig. 4.12(b), of these layers indicates that the interface intermixed region is \( \approx 1 \) nm and that a metastable equilibrium concentration of Ti-15Nb has developed within the Ti layers.

A set of compositional contour maps from Fig. 4.12(b) are plotted in Fig. 4.13(a) and 4.13(b). These profiles reveal that the interfaces of the multilayers are relatively compositionally sharp as previously observed in TEM cross-section micrographs. Any large contour increases within the plane are most likely due to a reconstruction artifact of the software. If a data point of a similar composition exists sufficiently out-of-plane, the mapping software will extrapolate the data to that point producing an artificial hump in the contour plane. In each example, these artifacts are minimal and the compositional interfaces appear uniform.

4.4.2 Atom Probe Discussion

The interdiffusion of Nb into the Ti layers is quite surprising and is not believed to be an artifact of the evaporation process due to the shape of the compositional profile curves in Fig. 4.12(b). If element A in an A/B multilayer evaporates faster then B, then as A is field evaporated completely from the tip, the immediate layer of B (under A) at the tip’s apex will be preferentially retained due to its lower field evaporation rate. This generates a local density variation in B near the interface [12]. Such field evaporation artifacts can appear as saw-tooth type profiles in compositional verses depth plots [11]. The bell-shaped curvature of the composition profile in Fig. 4.13(b) does not suggest that this type of artifact is present.
Furthermore the constant level of Nb within the Ti layer would not be expected to be maintained evenly throughout the layer if it was a density variation artifact. The slight asymmetry (slope) of the profile curves on either side of the interface could be a result of the different evaporation rates.

The relatively even composition of Ti-15Nb over ≈ 2 nm of length for each Ti layer is indicative of an equilibrium composition. The equilibrium thermodynamic phase diagram for Ti-Nb [12] does not provide any phase field boundaries to suggest that Ti-15Nb is a particular equilibrium condition or intermetallic precipitate for these materials. The Ti-15Nb composition places it into the $\alpha$ (hcp) + $\beta$ (bcc) phase field at room temperature.

Recently Zhang et al. [16] reassessed the Ti-Nb phase diagram. They have surveyed the literature and reported that Ti’s $\beta/(\alpha+\beta)$ transus phase boundary has considerable scatter with Nb concentration ranging from 0~35 at%, 6~20 at.%, and 0~25at.% depending upon processing parameters and cooling rates [16]. Since this multilayer was shown to be on the biphase stability boundary, the presence of the Ti-15Nb metastable equilibrium concentration could be a result of some type of $\beta$ transus thermodynamic driving force. It is unclear if the thermodynamic driving force of a $\beta$ transus is sufficient for diffusion. But the interdiffusion of Nb into Ti thermodynamically stabilizes the bcc Ti phase. This multilayer was deposited in a region that is near bcc Ti stabilization on the biphase diagram. The lack of diffusion of Ti into the Nb layer would destabilize the bcc / bcc phase structure of the multilayer. This can be seen in the solution thermodynamic volumetric free energy change of Ti with Nb content in Fig. 4.14. Furthermore the similar atomic radii of Ti (0.140 nm) and Nb (0.145
nm) [23] coupled to the stabilize\( \text{bcc} \) structure between the two layers could help to facilitate the enhanced interdiffusion of Nb into the \( \text{bcc} \) Ti layers.

It is noted that in the specimen preparation of the atom probe tips (Section 2.5.1), each tip was heated to approximately \( 80^\circ \text{C} \) – \( 100^\circ \text{C} \) for one hour to cure the silver conductive epoxy. This necessary heating step could be a contributing mechanism for accelerating the interdiffusion of the two layers. But it does not explain the metastable equilibrium composition of Ti-15Nb. This atom probe preparation technique has been used for other specimens with similar melting temperatures (diffusivities) that did not indicate any substantial diffusion within the layers [14].

The calculated volumetric free energy change of Ti with Nb content [21] is plotted in Fig. 4.14. The addition of Nb reduces \( \Delta G_{\text{Ti}} \). This is consistent with Nb being a \( \text{bcc} \) \( \beta \)-stabilizer for Ti alloys. Based upon the equilibrium thermodynamic calculation, the additional 15 at.% Nb content would not completely drive the \( \text{hcp} \) Ti phase to the \( \text{bcc} \) Ti phase but reduce the \( \Delta G_{\text{Ti-15Nb}} \) value to \( \approx 1.0 \times 10^8 \text{ J/m}^3 \). Coupling this refined \( \Delta G_{\text{Ti-15Nb}} \) to the slope of the \( \text{hcp} \) Ti / \( \text{bcc} \) Nb – \( \text{bcc} \) Ti / \( \text{bcc} \) Nb boundary in Fig. 4.1(b), the interfacial energy reduction, \( \Delta \gamma_{\text{bcc/bcc}} \), was \( \approx -265 \text{ mJ/m}^2 \). Interestingly, this value is in much closer agreement to \( \Delta \gamma_{\text{bcc/bcc}} \) of Zr/Nb and the predicted \( \Delta \gamma_{\text{bcc/bcc}} \) for Ti/Nb using the van der Merwe interfacial energy model (\( \Delta \gamma_{\text{bcc/bcc}} = -280 \text{ mJ/m}^2 \)) of Section 4.2.2. This refined free energy calculation being in close agreement to the predictions is additional evidence that Nb has interdiffused into the Ti layers resulting in a facilitation of pseudomorphic \( \text{bcc} \) Ti at a much larger layer thickness for the Ti/Nb multilayers.
Fig. 4.14 Equilibrium volumetric free energy change of Ti with Nb concentration.
To estimate the interdiffusion coefficient, the Matano Method [15] has been applied. The normalized composition profile for one bilayer of the Ti/Nb multilayer is plotted in Fig. 4.14(a). The plane of Matano has also been marked. Curve fitting the interface’s compositional curve, the chemical interdiffusion coefficient, $\tilde{D}$, was determined by

$$
\tilde{D} = \frac{1}{2t} \frac{\delta x}{\delta c_{\text{Nb}}} \int_{c_{\text{Nb}'}}^{c_{\text{Nb}}} x dc
$$

(4.9)

where $t$ is the time for diffusion (taken to equal the total time for deposition of the multilayer, 5200 sec), $\delta x/\delta c_{\text{Nb}}$ is the inverse of the slope of the composition curve, $c_{\text{Nb}}$ is the concentration of Nb at a distance $x$ from the plane of Matano, and $c_{\text{Nb}'}$ is the constant concentration of Nb far from the plane of Matano. The calculated diffusivities are plotted in Fig. 4.14(b). The diffusivity is on the order of $10^{-22}$ cm$^2$/sec. Though this value is high for bulk diffusion at room temperature, it is on the order of typical diffusivities reported for thin film multilayers [17]. DuMond and Youtz [18] reported room temperature diffusivity of $\sim 5 \times 10^{-20}$ cm$^2$/sec for Cu/Au multilayers with a bilayer spacing of 10 nm.

The interdiffusion in thin films at much lower temperatures than bulk diffusion couples is due to the cleanness of the film’s interfaces (grown in UHV conditions), the fine-grain microstructure which can be highly defective and have numerous grain boundaries, and the short diffusion distances between layers [17]. Additionally, Thornton [19] has estimated the arrival energy of sputtered Ti and Nb atoms to be 20 eV/atom and 8 eV/atom respectively. The growing layers rapidly dissipate this heat when one considers atomic vibrations to be on the order of $10^{12}$ Hz, but the arrival energy coupled with the rate of deposition could facilitate diffusion if a chemical non-equilibrium exists between the layers. The deposition rate of this multilayer was $\approx 1.0$ Å/sec at 100 W.
Fig. 4.15 (a) Normalized Ti-15Nb compositional profile of one bilayer from Fig. 4.13(b). The plane of Matano has been marked and used in calculating the diffusion coefficient across the interface. (b) The chemical interdiffusion coefficient from (a) as a function across the interface.
As will be discussed in Chapter 6, future work in depositing additional Ti/Nb multilayers at a various bilayer spacings and various volume fractions of Nb are required to better determine the degree of interdiffusion as a function of length scale and phase stability. The metastable equilibrium concentration of Nb into Ti is perplexing. Rather than exponentially decaying within the Ti layer, the Nb interdiffusion has established a metastable equilibrium concentration across the entire Ti layer. This equilibrium condition may be a result of a driving force of a $\beta$-transus stability condition with Nb. The use of 3DAP in characterizing this multilayer has provided additional insight into the chemical arrangement that is occurring at this length scale. The significant interdiffusion of Nb is a sufficient factor for reducing the interfacial energy in facilitating the hcp to bcc phase stability in Ti at a fairly large bilayer spacing.

4.5 Engineering Phase Stability in Ti/Nb Multilayers

The successful application of classical thermodynamic quantities to predict phase stability at a non-classical length scale has been accomplished. It should then be possible to use classical thermodynamic alloying techniques to engineer the phase stability boundaries. Hugosson et al. [20] have recently proposed a theoretical treatment of enhanced mechanical strength in multilayered films by using alloying to tune the phase stability. Recall that the slope of the biphase stability boundary, as shown in Eq. (4.2) and (4.7), is simply the ratio of the volumetric and interfacial free energies. The use of $\alpha$ (hcp) or $\beta$ (bcc) stabilizing elements for Ti would alter these free energy values. Consequently, this will change the slope of the
biphase stability boundary and a corresponding change in the critical transition thickness for the $hcp$ Ti – $bcc$ Ti phase fields. This was unintentionally observed between the predicted and experimental $hcp/bcc$ - $bcc/bcc$ boundary due to Nb’s interdiffusion into the Ti layers. For this study, intentional alloyed amounts of V, a $bcc$ β-stabilizer for Ti alloys, have been added to the Ti layer to engineer the phase stability boundary.

A series of Ti-8V/Nb multilayers were sputter deposited. Alloy percentages are given in atomic percent content. The alloy Ti-8V sputtering target was prepared by measuring the appropriate Ti and V powders and vacuum arc melting them into a ingot. The ingot was re-melted an additional two times from each side to ensure compositional homogeneity. The ingot was subsequently pressed into a target and machined into the required dimensions for installation into the sputtering guns.

To predict the change in slope with alloy content, a CALPHAD approximation to $\Delta G_{Ti-8V}$ [9] was used and whose value is listed in Table 4.2. For a first approximation to the predicted $hcp$ to $bcc$ Ti-8V phase stability boundary, the interfacial free energy in Table 4.2 was set to be equivalent to the $\Delta \gamma_{bcc/bcc}$ for Ti/Nb. The predicted slope, using Eq. (4.2), has been plotted in Fig. 4.16. With the addition of V, the facilitation of $bcc$ phase stability in multilayer system is seen by the suppression of the phase stability boundary for $hcp$ to $bcc$ Ti.

### 4.5.1 Results of Phase Engineering

Prior to the deposition of the Ti-8V/Nb multilayers, a monolithic 600 nm thick Ti-8V film was sputter deposited. The XRD scan from this Ti-8V film, shown in Fig. 4.17,
Fig. 4.16 Plot of the facilitation of hcp to bcc phase stability in Ti for Ti-8V/Nb multilayers as compared to unalloyed Ti/Nb.
Fig. 4.17 Reflection XRD pattern a monolithic 600 nm thick Ti-8V thin film. A super-solid-saturation $\alpha$-Ti was grown. This is indicated by the lack of any diffracted intensities of from any other phases, i.e. no split in the textured peak of {0002}. 

Intensity (arb. units) 

$\theta$ (degrees) 

20 (degrees) 

{0002} Ti
Fig. 4.18 A biphase stability diagram with the deposited Ti-8V/Nb multilayers. A facilitation of the hcp to bcc phase stability in the Ti layer has occurred.

Table 4.5 Deposited Ti-8V/Nb multilayers
indicates the film deposited as a super-solid saturation of α-Ti. There was no evidence of bcc phase formation in the XRD pattern, i.e. no splitting of the \{0002\} and \{011\} peak near 38°.

The deposited Ti-8V/Nb multilayers, as with the previous Ti/Nb films, grew with a preferred growth texture from the substrate of the closest packed planes of {0002} for the hcp phase and {011} for the bcc phase. The sputtered deposited Ti-8V/Nb multilayers are listed in Table 4.5 and plotted in Fig. 4.18.

4.5.2 Discussion of Phase Engineering

The addition of the V to the Ti layers has altered the critical transition thickness for hcp – bcc phase stability in Ti for Ti/Nb multilayers. β-stabilizers have a low solid-solubility (typically 1-2 at.%) in the standard state [12]. This low solubility in the equilibrium single-phase field of α-Ti would prevent a sufficient addition of β-stabilizer to the Ti layers in order to affect an experimentally observable change in the slope of the stability boundary. The addition of the 8 at.% V to the Ti layer was to ensure that the volumetric free energy change with alloying would be significant for an experimentally observable change in slope. However, if the large addition of a β-stabilizer would lead to the precipitation of a secondary phase in the monolithic Ti(V) film, the thermodynamics would become more complicated. The additional interfacial and volumetric free energies involved with a second phase precipitate would need to be accounted for in the framework of Eq. (4.1). Fortunately, the
Fig. 4.19 (a) Reflection XRD pattern for Ti/Nb multilayer #5 that diffracts the hcp / bcc structure (b) Reflection XRD pattern for Ti-8V/Nb multilayer #18 that diffracts the bcc / bcc structure. (c) Plan-view electron diffraction of Ti-8V/Nb multilayer # confirming the bcc / bcc structure.
monolithic Ti-8V film deposited as a supersaturated solid-solution of single phase \( \alpha \)-Ti. The increased solubility of V in \( \alpha \)-Ti could be a consequence of the rapid quench rates involved during sputter deposition [13].

From Fig. 4.18’s Ti-8V/Nb multilayer #18, it is evident that the addition of the \( \beta \) stabilizer has facilitated the \( bcc \) phase stability. Fig. 4.19(a) is the reflection XRD pattern for the \( hcp \) Ti / \( bcc \) Nb multilayer #5 in Fig. 4.18. This film has a bilayer thickness of 7.5 nm with \( f_{Nb} = 0.51 \). The XRD pattern exhibits the textured peaks of both \( hcp \) \{0002\} and \( bcc \) \{011\}. A similar multilayer of Ti-8V/Nb, with a bilayer spacing of 7.4 nm and a \( f_{Nb} = 0.50 \), has been deposited. Its reflection XRD pattern in Fig. 4.19(b) is consistently index as a \( bcc / bcc \) structure by the presence of a single \{011\} peak. The \( bcc / bcc \) structure has been verified by plan-view electron diffraction in Fig. 4.19(c). The alloyed multilayer, being at a nearly equivalent position on the biphase diagram as the unalloyed multilayer clearly demonstrates that the bcc phase stability has been altered.

The \{011\} XRD peak of the \( bcc/bcc \) alloyed specimen has shifted to slightly lower d-spacing of 2.319 Å compared to the unalloyed transformed \( bcc \) \{011\} peak of 2.33 Å observed in Section 4.2.1. This d-spacing shift is consistent with a reduction in the \( bcc \) \( a \)-lattice parameter from the alloy addition of V (3.03 Å) by Vegard’s Law. The alloy addition has shown that phase engineering of the \( hcp-bcc \) transformation in Ti is possible by alloying additions.
4.6 Summary

The $hcp$-$bcc$ transformation in Ti layers for Ti/Nb multilayers has been predicted and modeled by the use of a classical thermodynamic energies. Similar to Zr/Nb, the Ti layer, upon a change in phase stability has adopted its $\beta$-Ti lattice parameter. This lattice parameter is coherent with the $bcc$ Nb interface with negligible coherency strains. The critical transformation thickness for the $hcp$-$bcc$ transformation in the Ti layers in Ti/Nb multilayers is substantially larger than that of the Zr layers in the Zr/Nb multilayers. This has been rationalized using a simple van der Merwe interfacial energy model. 3DAP has also indicated that the Nb has interdiffused into the Ti layer helping to facilitate the transformation. This simple interfacial energy model predicted the interfacial energy reduction for Zr/Nb quite well. Refining the $\Delta G_{Ti(Nb)}$ with the atom probe results brought the experimentally determined interfacial energy reduction for Ti/Nb closer to the predictions of the van der Merwe model.

The stabilization of $hcp$ Nb was predicted and experimentally confirmed in Ti/Nb. The $hcp$ Nb phase in Ti/Nb had the same lattice parameters as the $hcp$ Nb phase in Zr/Nb. In each $hcp$ Nb example, the $hcp$ phase has formed a semi-coherent interface with Zr or Ti suggesting that the interfacial free energy reduction, and not coherency strains, are responsible for the stabilization of this novel phase.

3DAP characterization has been performed on a $bcc$ Ti/ $bcc$ Nb multilayer. These results have indicated that Nb has an interdiffused into the Ti layer to a metastable equilibrium composition. Finally, the use of alloying Ti with a $\beta$-stabilizer has been successful in engineering the phase stability.
References for Chapter 4


CHAPTER 5

SUPERCONDUCTIVITY & MECHANICAL PROPERTIES
OF ZIRCONIUM / NIOBIUM MULTILAYERS

5.1 Introduction

As alluded to in Chapter 1, the change in phase stability for individual layers within a multilayer could have a marked influence upon the physical properties for these materials. In this chapter the superconductivity and mechanical properties for Zr/Nb multilayers are reported. This work has been done to provide the future framework for additional studies on the relationship of phase stability and functional properties of multilayers.

5.2 Superconductivity in Zr/Nb Multilayers

Nb and Zr are superconducting metals with a critical transition temperature, $T_c$, of 9.2 K and 0.6 K respectively. This $T_c$ temperature can be increased up to 11 K for a chemically disordered $\text{Nb}_{0.75}\text{Nb}_{0.25}$ alloy [1]. Similarly, it has also been shown that depositing layers of a superconducting (S) and normal metal (N) in a multilayered stack can alter the $T_c$. In an S/

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N synthetic layered arrangement, where S is superconductive and N is a normal conductor, the superconducting metal experiences a proximity effect [2] in altering the $T_c$. The minimal temperature of the SQUID used in the $T_c$ measurements is 1.8 K, thus Zr will remain as a normal conductor. The proximity effect is the averaging phenomenon of the paring of electrons, referred to as Cooper pairs, which provide the superconducting current between two separated superconducting materials. A comprehensive review of the proximity effect in superconducting multilayers can be found in reference [3]. This averaging is achieved due to the relatively long coherence lengths (50-1000 Å) of the Cooper pairs. The result of the proximity effect causes a lowering of the $T_c$ to an intermediate $T_c$ temperature between the two materials.

Originally proposed by Cooper [4] and subsequently modified by de Gennes [5], the basic formulation for calculating the $T_c$ of an S/N system in which the layer thickness is smaller than the coherence length is

$$T_{c,NS} = \frac{\theta_D}{1.45} \exp \left[ -1/(N(0) V_{eff}) \right]$$

(5.1)

where $\theta_D$ is the Debye temperature and $N(0)V_{eff}$ is the effective attractive term given as

$$[N(0)V]_{eff} = \frac{N^{2}_{Nb}V_{Nb}d_{Nb} + N^{2}_{Zr}V_{Zr}d_{Zr} + N^{2}_{i}V_{i}d_{i}}{N_{Nb}d_{Nb} + N_{Zr}d_{Zr} + N_{i}d_{i}}$$

(5.2)

where $d_{Nb}$, $d_{Zr}$, and $d_{i}$ are the thicknesses of the Nb, Zr, and interface layers respectively. de Gennes originally did not propose the $d_{i}$ interface thickness term but assumed an infinitely sharp interface. The interface thickness, added by Lowe and Geballe [6], is an experimental reality formed by the intermixing of A/B at the interface and can have a substantial effect on $T_c$. 

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5.2.1 Superconducting Results

The experimental methods for the superconductivity experiments have been described in detail in Chapter 2 Section 2.6.1. The $T_c$ data for the Zr/Nb multilayers has been divided into different categories depending on whether the thickness of the Nb layer ($t_{Nb}$) is kept constant, or thickness of the Zr layer ($t_{Zr}$) is constant, or the fraction of Nb ($f_{Nb}$) in the multilayer is kept constant.

Fig. 5.1 shows a plot of $T_c$ versus $t_{Nb}$ for a constant value of $t_{Zr}$=1.2 nm. The experimental data points are marked as circles on this plot. In addition to the experimental data in Fig. 5.1, the calculated $T_c$ as a function of $t_{Nb}$ with $t_{Zr}$ = 1.2 nm and $d_f$=0 from Eq. (5.1) has been plotted as a solid line for comparison. The trend in the experimental data suggests that with increasing Nb layer thickness, the $T_c$ will be increased provided that the Zr layer thickness is kept constant. The predicted trend appears to be in good agreement with the experimental values, especially for smaller values of $t_{Nb}$. For larger values of $t_{Nb}$ ($\approx$ 8 nm), the experimental value is in excess of the calculated value. Possible reasons for this difference between the calculated and experimentally determined values include the presence of an intermixed layer or an inaccurate measurement of the Zr layer thickness such that the actual value of $t_{Zr}$ is smaller, either of which can raise the value of $T_c$ for the multilayer.

Fig. 5.2 shows two sets of experimental data exhibiting the variation in $T_c$ with changing Zr layer thickness with the Nb layer thickness remaining constant. One set of data corresponds to $t_{Nb}$ = 4 nm while the second set corresponds to $t_{Nb}$ = 0.8 nm. For both sets of data, with increasing $t_{Zr}$, $T_c$ for the multilayers decreased. Good agreement between experiment and prediction existed for the $t_{Nb}$ = 4 nm. For the $t_{Nb}$ = 0.8 nm, the experimental
**Fig. 5.1** $T_c$ for a varying $t_{Nb}$ but constant $t_{Zr}$. The circles are the experimental data points where the solid line is the predicted trend for zero intermixing at the interface.

**Fig. 5.2** $T_c$ for varying $t_{Zr}$ but constant $t_{Nb}$. The circles are the experimental data points where the solid line is the predicted trend for zero intermixing at the interface.
T\textsubscript{c} was significantly larger than the calculated value. As discussed earlier, a possible reason for this difference is the inaccurate measurement of t\textsubscript{Nb}. Therefore, an attempt has been made to fit the experimental data by using t\textsubscript{Nb} as a fitting parameter. The result shows that for t\textsubscript{Nb} = 1.2 nm, there is a much better agreement between the calculated and experimental values of T\textsubscript{c}.

The calculated variation in T\textsubscript{c} as a function of the bilayer thickness (\(\lambda\)), for a constant volume fraction, \(f\textsubscript{Nb} = 0.5\) and intermixed layer, \(d\textsubscript{i}\), has been plotted in Fig. 5.3. Additionally, the predicted trends of T\textsubscript{c} with increasing intermixing has been added to the plot. It is interesting to note on Fig. 5.3 that as the intermixed region, \(d\textsubscript{i}\), becomes thicker, there is a stronger variation of T\textsubscript{c} with \(\lambda\). For negligible intermixing (\(d\textsubscript{i} = 0\)), there appears to be no variation in T\textsubscript{c} with changing \(\lambda\). Based on the experimental measurements of T\textsubscript{c} listed in Table 5.1, it appears that for changing \(\lambda\) for the same \(f\textsubscript{Nb}\) there is no significant change in T\textsubscript{c}.

5.2.2 Superconductivity Discussion

The Zr/Nb multilayer’s T\textsubscript{c} properties followed reasonably well to the predictions of the proximity effect model. No notable deviations in T\textsubscript{c} were observed. Even though some of these multilayers, as listed in Table 5.1, have undergone a change in phase stability, this change was not sufficient enough to alter the T\textsubscript{c} from the predictions of the model. The proximity model only includes length scale and not phase stability changes in predicting the T\textsubscript{c} trend. The lack of T\textsubscript{c} changing for phase stability suggests that there is no significant difference in the density of states at the Fermi level for the two polymorphs [6]. Unlike Lowe and Geballe [6], who noted enhancement of T\textsubscript{c} with the formation of a coherent bcc Ti
Table 5.1 Superconducting critical transition temperature, $T_c$, tabulated with individual layer thickness and phase for Zr/Nb multilayers.

<table>
<thead>
<tr>
<th>Phase (Zr/Nb)</th>
<th>$t_{Zr}$ (nm)</th>
<th>$t_{Nb}$ (nm)</th>
<th>$T_c$ (K) +/- $T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp/bcc</td>
<td>500</td>
<td>500</td>
<td>9.12 +/- 0.24</td>
</tr>
<tr>
<td>hcp/bcc</td>
<td>1.29</td>
<td>7.95</td>
<td>8.7 +/- 0.30</td>
</tr>
<tr>
<td>hcp/bcc</td>
<td>1.29</td>
<td>7.95</td>
<td>8.5 +/- 0.22</td>
</tr>
<tr>
<td>hcp/bcc</td>
<td>1.32</td>
<td>3.98</td>
<td>7.5 +/- 0.30</td>
</tr>
<tr>
<td>hcp/bcc</td>
<td>2.54</td>
<td>2.54</td>
<td>6.9 +/- 0.25</td>
</tr>
<tr>
<td>hcp/bcc</td>
<td>4.1</td>
<td>1.0</td>
<td>4.4 +/- 0.40</td>
</tr>
<tr>
<td>hcp/bcc</td>
<td>2.45</td>
<td>1.02</td>
<td>4.8 +/- 0.44</td>
</tr>
<tr>
<td>hcp/hcp</td>
<td>2.76</td>
<td>0.74</td>
<td>3.6 +/- 0.44</td>
</tr>
<tr>
<td>hcp/hcp</td>
<td>4.25</td>
<td>0.75</td>
<td>3.2 +/- 0.40</td>
</tr>
<tr>
<td>bccβ/bcc</td>
<td>0.53</td>
<td>3.87</td>
<td>8.35 +/- 0.40</td>
</tr>
<tr>
<td>bccβ/bcc</td>
<td>0.53</td>
<td>3.87</td>
<td>8.40 +/- 1.4</td>
</tr>
<tr>
<td>bcc/bcc</td>
<td>1.19</td>
<td>1.24</td>
<td>6.30 +/- ---</td>
</tr>
<tr>
<td>bcc/bcc</td>
<td>0.68</td>
<td>1.42</td>
<td>2.55 +/- ---</td>
</tr>
</tbody>
</table>
no such enhancement was observed for these multilayers. Lowe and Geballe [6] concluded that their enhancement was due to a solid-solution formation at the interface and subsequent XRD experiments confirmed that Zr had interdiffused into the Nb layer to a thickness of ≈ 1 nm for their sputtered deposited multilayers [6].

Fig. 5.3 is a plot of $T_c$ as a function of the bilayer thickness, $\lambda$, for a fixed $f_{Nb} = 0.5$. As predicted by Lowe and Geballe [6], increased intermixing at the interface will raise the $T_c$ for very thin bilayers. Unlike Lowe and Geballe’s enhanced $T_c$ experimental result[6] for a Zr/Nb multilayer, no significant change in $T_c$ for a change in $\lambda$ was observed for these samples. When the bilayer thickness was reduced from 5 nm to 2.4 nm for a $f_{Nb} \approx 0.5$ multilayer, the $T_c$ changed from 6.9 K to 6.3 K. This is a rather small difference (and reduction) in $T_c$ for a 50% decrease in $\lambda$. This experimental result are consistent with a multilayer with negligible intermixing. The experimental quality of the sputtered deposited multilayer’s interfaces could explain the differences the reported $T_c$ for this work in as compared to Lowe and Geballe [6].

5.3 Mechanical Properties of Zr/Nb Multilayers

The bulk modulus of the Zr/Nb multilayers was determined by nanoindentation. The experimental background and procedure have been discussed in detail in Chapter 2 Section 2.6.2. As the individual phases within the multilayer stack change, the local bonding is different and should generate a difference in the elastic modulus of the individual material.
Fig. 5.3 Predicted $T_c$ trends for increased intermixing at the interface for a Zr/Nb multilayer with $f_{\text{Nb}} = 0.5$. 
5.3.1 Elastic Modulus Results

Fig. 5.4 is a plot of the biphasic stability diagram for the Zr/Nb multilayers with the corresponding elastic modulus for each multilayer. Table 5.2 is a tabulation of the bulk elastic constants for Zr and Nb. The standard deviation for each modulus is within 10% of the averaged value. This indicates that the experimental data collection is good. For comparison, a simple rule of mixture, based upon the volume fraction of each constituent layer and Table 5.2’s values, has been placed underneath the experimental values. The majority of the films exhibited good agreement with the measured modulus to the rule of mixture approach. In the extreme Nb-rich region, the coherent $bcc$ Zr / $bcc$ Nb multilayer had a measurable enhancement of the modulus. The modulus values reported near the boundary for pseudomorphic phases tended to be larger than the predicted value whereas the bulk equilibrium phases near the boundary were slightly less than the predicted value.

5.3.2 Elastic Modulus Discussion

Reasonable agreement was achieved between the measurable modulus and the predictions from the rule of mixture approach. Interestingly, the best fit for the $bcc$ Zr / $bcc$ Nb rule of mixture modulus occurred for the coherent interfaces. The semi-coherent $bcc$ $\beta$-Zr / $bcc$ Nb interface had a slightly higher measured modulus than the prediction. This is peculiar because one could expect closer agreement in the calculated modulus for the $bcc$ $\beta$-Zr / $bcc$ Nb interface rather than the coherent $bcc$ Zr / $bcc$ Nb interface because each phase’s
Fig. 5.4 The elastic modulus with their respected position on the Zr/Nb biphase stability diagram. For comparison, in italics, a rule of mixture prediction of elastic modulus is given.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Elastic Modulus (GPa) [ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp α-Zr</td>
<td>98                          [20]</td>
</tr>
<tr>
<td>bcc β-Zr</td>
<td>46.7                        [9]</td>
</tr>
<tr>
<td>bcc Nb</td>
<td>104.9                       [20]</td>
</tr>
<tr>
<td>hcp Nb</td>
<td>97.7                        [8]</td>
</tr>
<tr>
<td>Si</td>
<td>113                         [20]</td>
</tr>
</tbody>
</table>

Table 5.2 Polycrystalline elastic modulus of Zr and Nb phases used in rule of mixture prediction. Si (substrate for all films) is referenced for comparison.
bonds are not being displaced for coherency. In the extreme Nb-rich coherent \textit{bcc Zr} / \textit{bcc Nb} multilayer, the modulus was significantly enhanced. This multilayer contains an approximately 0.5 nm Zr / 4.0 nm Nb layered structure. Other enhancements of the modulus have been reported in Cu/Pd [10], Cu/Ni [11-12,], and Ag/Pd [13] using a bulge tester. These materials were termed ‘super-modulus.’ Subsequently, the apparent enhancement of the modulus was found to be an experimental artifact [14]. Due to this initial confusion, considerable interest has been undertaken to measure the elastic modulus of the thin films. Enhancements, not as a sample artifact, have been observed in other systems such as Cu/Nb multilayers [15]. The most recent models to explain these anomalies have focused upon the large number of interfaces present at very small bilayers [16-18]. When the bilayers approach 2 nm for equal volume fractions, large elastic strains, 1%-2%, are sufficient to induce higher-order elastic effects [15]. Even though the 0.5 nm Zr / 4 nm Nb multilayer is not in the sub 2 nm bilayer regime, interface disorder, which can be a significant contributor in elastic anomalies [19], is suspected for the film. The 0.5 nm Zr thickness is in a region where sufficient interdiffusion at the interface can result. A change in the \textit{bcc} coherent lattice parameter has been observed (Table 3.2) that is on the order of 2.5% elastic strain. These contributing factors are suspected to be responsible for the non-linear anomalies of the elastic modulus.

Good agreement was observed between the measured and the rule of mixture values for the \textit{hcp Zr} / \textit{hcp Nb} multilayers. The calculated elastic modulus was taken from a set of first-principle calculations [9] which were based upon slightly different \textit{hcp} Nb lattice
parameters then those observed in this sample. Even with this small discrepancy, the estimated modulus matched well to the experimentally determined $hcp$ Nb elastic modulus.

5.4 Summary

Changes in the phase stability can have marked influences upon the physical properties of the multilayered thin film. The superconducting transport and mechanical properties for the Zr/Nb multilayers were investigated. Using a SQUID, the critical transition temperature, $T_c$, for the Zr/Nb multilayers was measured as a function of constant layer thickness and volume fraction. The predictions of de Gennes proximity model [5] for $T_c$ as a function of constant layer thickness of either the superconducting or normal metal layer matched well to the experimentally determined $T_c$’s. It is interesting that this model does not account for changes in phase stability yet data points that corresponded to pseudomorphic phases fit well to the predicted trends. This suggests that the Fermi energy between the polymorphic phases are similar. Unlike Lowe and Geballe [6], an enhancement of the $T_c$ for a reduction in the bilayer thickness was not observed for the $bcc$ Zr / $bcc$ Nb bilayers. Lowe and Geballe [6] explained their $T_c$ increase as the development of an intermixed solid solution interface region. This is consistent with $T_c$ increases observed in Nb-Zr bulk alloys. The lack of an increase in $T_c$ for the multilayers grown in this study suggests that the interfaces are more abrupt and less intermixed.

The elastic modulus of the Zr/Nb multilayers was determined by nanoindentation. The measured modulus values matched reasonable well with predictions using a simple
rule of mixture approach. An enhancement of the modulus for extreme Nb-rich coherent \( bcc \) Zr / \( bcc \) Nb was observed and is suspected to be a result from a disordered interface with large elastic coherent strains.
References for Chapter 5

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

Phase stability in thin films and multilayers has been of considerable interest to the materials science and physics community. Many of the pseudomorphic thin film phases reported in the literature have been discovered serendipitously. This work, for the first time, has used a classical thermodynamic description of phase stability in multilayers in predicting and confirming pseudomorphic phase stability. The classical thermodynamic model represents the interplay of volumetric and interfacial free energy reduction in determining phase stability. Though these terms are simple, they have been quite powerful in their predictions at a non-classical length scale. An outcome of the classical thermodynamic model has been the biphase stability diagram. This diagram visually represents the two degrees of freedom, the length scale, given as the bilayer thickness, and the volume fraction of one of the constituent layers in establishing the phase stability boundaries.

Using the biphase diagram and a single reported hcp to bcc transformation in Zr for Zr/Nb multilayers, additional hcp to bcc transformations were predicted and subsequently confirmed for Nb-rich volume fractions and various bilayer thicknesses in Zr/Nb. Plan-view electron diffraction, transmission XRD, and reflection XRD characterization techniques
confirmed these changes in phase stability. Zr initially formed its $\text{bcc} \beta$-Zr lattice parameter upon transformation. This indicates that a reduction in interfacial free energy, and not coherency strains, drove the change in phase stability. Upon further reduction in bilayer thickness for a fixed volume fraction, $\beta$-Zr became coherent with $\text{bcc}$ Nb. The establishment of a coherency boundary has been plotted on the biphase stability diagram. Using an O-lattice approach, the structural component of misfit dislocations to the interfacial energy has been estimated for the $\text{hcp}$ Zr / $\text{bcc}$ Nb to $\text{bcc} \beta$-Zr / $\text{bcc}$ Nb to $\text{bcc}$ Zr / $\text{bcc}$ Nb phase stability changes. Additionally, the chemical component was assessed using a thermodynamic approximation to the excess bond energy.

The successful confirmation of additional $\text{hcp}$ to $\text{bcc}$ phase stability in Zr for Zr/Nb allowed for the prediction of a novel $\text{hcp}$ Nb phase for Zr-rich volume fraction Zr/Nb multilayers. Unlike Zr that exhibits an allotropic phase transformation from $\text{hcp}$ to $\text{bcc}$ on its equilibrium phase diagram, $\text{hcp}$ Nb is not an equilibrium phase for this material. Using a predicted $\text{hcp}$ Zr / $\text{hcp}$ Nb phase field on the biphase stability diagram, a series of Zr/Nb multilayers were sputtered deposited. As predicted, an $\text{hcp}$ Nb phase field did exist. $\text{hcp}$ Nb, upon a change in phase stability, adopted its own independent lattice parameters. This confirms that interfacial energy reduction and not coherency strains are responsible for the change in phase stability.

Titanium is chemically similar to Zr in that each material has an allotropic phase transformation from $\text{hcp}$ to $\text{bcc}$ at elevated temperatures. Based upon such similarities, $\text{hcp}$ to $\text{bcc}$ Ti phase stability should be possible for Ti/Nb multilayers. A series of Nb-rich volume fraction multilayers were sputtered deposited. Subsequently a change in $\text{hcp}$ to $\text{bcc}$
Ti phase was confirmed by electron and x-ray diffraction and plotted on a biphase stability diagram. Similar to Zr, the Ti layers, upon transformation to $bcc$, adopted the high temperature $bcc \beta$ lattice parameter. This lattice parameter is nearly identical to $bcc$ Nb and the coherency strains were negligible. The critical thickness for $hcp$ to $bcc$ phase stability in Ti was significantly larger for Ti/Nb than for Zr in Zr/Nb for a similar volume fraction. Using a van der Merwe interfacial energy model, the reduction of the misfit to zero for $bcc \beta$-Ti / $bcc$ Nb upon transformation allowed for an overall greater reduction in interfacial energy as compared to $bcc \beta$-Zr / $bcc$ Nb. This larger reduction in interfacial energy provided a greater contribution to the driving force for transformation. Similar to Zr/Nb, in the Ti-rich volume fraction Ti/Nb multilayers stabilized $hcp$ Nb with $hcp$ lattice parameters equivalent to the $hcp$ Nb lattice parameters indexed in $hcp$ Zr / $hcp$ Nb.

The chemical composition of the Ti/Nb multilayers was characterized using Atom Probe Tomography. The high spatial resolution of this technique allows for atomic level reconstruction of the chemistry at the interface and within the constituent layers. The results of the Ti/Nb multilayered film indicated an intermixed interface of $\approx$ 1 nm with significant interdiffusion of Nb to a metastable equilibrium concentration into the Ti layers. It is unclear from the equilibrium thermodynamic phase diagram for Nb-Ti why this concentration of Nb has been established. The driving force is suspected to be a $\beta$-transus. The diffusivity coefficient, determined by the atom probe compositional profile, is on the order of other reported diffusivity values for thin films reported in the literature. The presence of Nb, a $\beta$-stabilizer, is a significant thermodynamic driving force, along with the interfacial energy reduction, in stabilizing the $bcc$ Ti phase. Refinement of the $\Delta\gamma_{bcc/bcc}$ measured value with
the atom probe results indicated closer agreement of the interfacial energy reduction with predictions afforded by the van der Merwe interfacial model. Future work should be done in growing multiple Ti/Nb films at various bilayer spacings and volume fractions of Nb for atom probe analysis to better determine the driving force of Nb’s interdiffusion. Future atom probe specimen needles should be metals with high thermal conductivity at cryogenic temperatures to reduce field evaporation artifacts that are prevalent at the start of the atom probe experiment.

The successful use of classical thermodynamic quantities in the prediction of phase stability allowed for the use of traditional metallurgical alloying techniques to engineer the critical transition thickness. By alloying Ti with V, a bcc β-stabilizer, the free energies are altered for the bcc stabilization of Ti. As predicted, the hcp to bcc stabilization was facilitated by the addition of the β-stabilizer. Future work should be directed towards establishing the accuracy of CALPHAD or other type of energy calculations in predicting the change in phase stability with alloy content. Alternatively, work could be directed towards alloying Ti with hcp α-stabilizers that should suppress the hcp to bcc phase stability in Ti. The ability to predict and engineer phase stability allows for many novel possibilities in tuning the phase stability for a particular functional property.

Changes in phase stability should have marked influences on the physical properties of the multilayered thin films. The critical transition temperature, $T_c$, for superconductivity in Zr/Nb multilayers was determined as a function of constant layer thickness and volume fraction. The change in $T_c$ increased for increasing Nb layer thickness for constant Zr layer thickness. An opposite trend was observed for increasing Zr layer thickness for constant
Nb layer thickness. These results were consistent with the proximity model in Chapter 5. It is interesting to note that this model does not account for phase stability changes but still had relatively good agreement with the experimental data. No enhancement of $T_c$ with the formation of a coherent $bcc$ Zr / $bcc$ Nb interface was observed. The lack of an increase in $T_c$ for these multilayers suggests that the interfaces are abrupt.

Finally, the elastic modulus for the Zr/Nb multilayers was measured using nanoindentation. The values matched reasonably well with predictions afforded by a simple rule of mixture of the elastic modulus values. An enhancement of the modulus was observed for the coherent $bcc$ Zr / $bcc$ Nb multilayers in the extreme Nb-rich volume fraction section of the biphase stability diagram. The extreme ratio in thickness for the individual layers coupled by a large elastic strain is suspected to be the contributing factor. Future experimental and modeling effort in this region of phase stability is required to develop a detailed understanding of this phenomenon.

In conclusion, the experimental prediction and confirmation of phase stability in Zr/Nb and Ti/Nb multilayers has been successfully demonstrated. Some simple modeling to explain the contributing energies has been undertaken. The refinement of the classical thermodynamic energies, such as first principle calculations, could be used in these models to provide additional understanding of the phase stability energies. Further study is required to understanding the chemical profile at the interface and within the individual layers. The atom probe results of Nb’s significant interdiffusion in Ti was unexpected and demonstrates the complexities of various energetic contributions to phase stability. Finally, the successful use of alloying to manipulate phase stability at the nanoscale has been demonstrated.
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