Dimensionally Induced Structural transformations in Titanium-Aluminum Multilayers

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Ti/Al multilayered thin films with a range of bilayer thicknesses have been fabricated by dc magnetron sputtering and characterized by transmission electron microscopy and high resolution electron microscopy. A series of structural transitions in the form of changes in the stacking sequence of the closed packed atomic planes in the Ti and Al layers have been observed as a function of the bilayer thickness. A possible explanation for these transitions based on the model initially proposed by Redfield and Zangwill is presented in this Letter. [S0031-9007(96)00213-X]

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Synthetically modulated structures, like multilayered thin films, exhibit interesting magnetic and electronic properties. Consequently, there has been a considerable effort directed towards the study of these properties. Much less effort has involved the investigation of the structural and phase transitions occurring in such thin films [1,2].

In this Letter, the mechanism underlying a series of novel structural transitions occurring in titanium/aluminum thin film multilayers [3,4] has been addressed. These transitions are dimensionally induced in the multilayers as the compositionally modulated wavelength, referred to here as the bilayer thickness, of the multilayers is reduced (from $\approx$20 to 5 nm). At room temperature, bulk Ti and Al have hcp and fcc crystal structures, respectively. However, in the thin film form, multilayers of Ti/Al exhibit very interesting structural transitions as the bilayer thickness decreases. Ti transforms from hcp to fcc. Al, on the other hand, transforms from fcc to hcp within the range of bilayer thicknesses studied. An attempt was made to rationalize some of these observations on the basis of the model proposed by Redfield and Zangwill [5] for predicting stacking sequences in closed packed metallic superlattices. Schechtman, van Heerden, and Josell [6] have published results of similar structural transitions in Ti/Al multilayers, but attributed their results to artifacts introduced by sample preparation techniques. In their work, they studied multilayer samples with considerably larger bilayer thicknesses ($\approx$30 nm) than those to which reference is made above (i.e., [3,4]). With such large bilayer thicknesses, it is unlikely that the model of Redfield and Zangwill [5] is appropriate. However, it is important to determine whether at smaller bilayer thicknesses, such a structurally sensitive model does apply. This determination is the subject of the present Letter.

The Ti-Al multilayers were fabricated in a custom designed UHV magnetron sputtering apparatus. The base pressure prior to sputtering was 7×10^{-9} torr and argon pressure during sputtering was 2 mtorr. Ti was sputtered using 200 W and Al using 160 W of dc power, corresponding to a sputtering rate of close to 0.1 nm/sec for both Ti and Al. The multilayers were deposited on oxidized (100) silicon wafers. The substrate temperature during deposition did not exceed 45 °C. The individual thicknesses of Ti and Al layers were nominally equal. Structural characterization of the multilayers was done using transmission electron microscopy (TEM). The details of cross-section TEM sample preparation are given elsewhere [7]. Specimens were examined in a JEOL 200 CX TEM and a Hitachi 9000NAR TEM operating at accelerating voltages of 200 and 300 kV, respectively.

The bilayer thicknesses for the multilayers which have been studied are 108, 21, 9.8, and 5.2 nm. A selected area diffraction (SAD) pattern obtained from a cross section of the 108 nm multilayer is shown in Fig. 1. The reflections

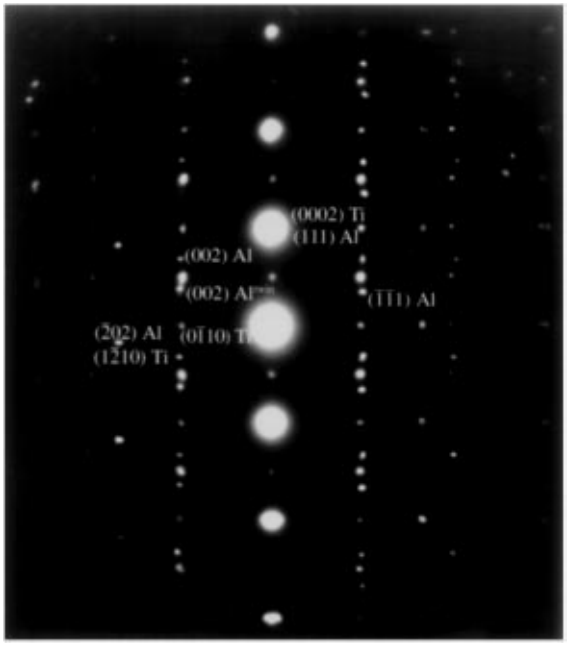

FIG. 1. SAD pattern from the cross section of the multilayer which has a bilayer thickness of 108 nm. The spots in the SAD pattern correspond to the $\langle 2\bar{1}\,\bar{1}0\rangle$ and $\langle 10\bar{1}0\rangle$ zone axes for hcp Ti and the $\langle 1\bar{1}0\rangle$ and $\langle 1\bar{2}1\rangle$ zone axes for fcc Al.

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in the SAD pattern correspond to the $\langle 2\bar{1}\,\bar{1}0\rangle$ and $\langle 10\bar{1}0\rangle$ zone axes for hcp Ti and the $\langle 1\bar{1}0\rangle$ and $\langle 1\bar{2}1\rangle$ zone axes for fcc Al indicating that the Ti and Al layers grow with a {0002} and {111} texture, respectively, parallel to the substrate. At this value of bilayer thickness both Ti and Al retain their bulk stable crystal structures resulting in a stacking sequence of hcp Ti/fcc Al. Figure 2 shows a HRTEM image from a cross section of the 21 nm multilayer showing clear evidence of the presence of fcc Ti regions in the hcp Ti layers; SAD patterns (not shown here) contain reflections consistent with this observation [4]. Reducing the bilayer thickness to 21 nm results in a stacking sequence of (fcc Ti + hcp Ti)/(fcc Al). The proportion of fcc Ti in the Ti layer is significantly smaller than that of hcp Ti in the same layer as indicated by diffraction evidence [3]. An HRTEM image from the 9.8 nm multilayer (Fig. 3) shows that the Ti layers have transformed completely into an fcc lattice resulting in a stacking sequence fcc Ti/fcc Al. Further reduction of the bilayer thickness to 5.2 nm results in transitions occurring in both the Ti and Al layers. A cross-sectional HRTEM image from this multilayer, shown in Fig. 4, indicates a stacking sequence hcp Ti/hcp Al. The results are tabulated in Table I.

It is possible to transform an fcc ABCABC... stacking sequence into an hcp ABABAB... stacking sequence or vice versa by introducing successive intrinsic stacking faults in the atomic layers of the parent structure. The Redfield-Zangwill model [5] calculates the potential $\mu(d)$ of a stacking fault as a function of its distance d from a bicrystal interface between two dissimilar metals given by

$$\mu(d) = \mu_b + \Delta F \Delta V_2 B(E_F) \times \sin\{2d\cos^{-1}[(E_F/6V_1) + 1] + \delta\}/d^2, \quad (1)$$

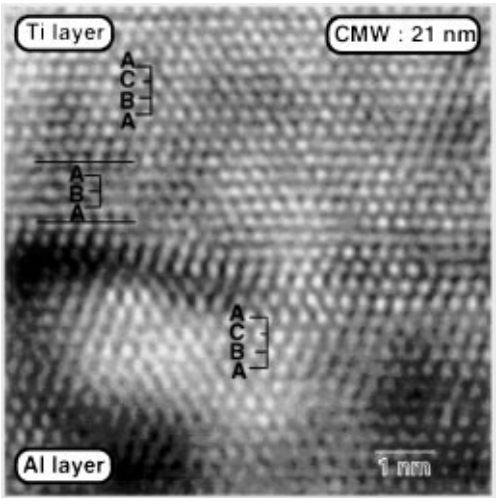

FIG. 2. HREM image from the cross section of the multilayer which has a bilayer thickness of 21 nm. It shows the fcc stacking sequence in the Al layer and the mixed fcc + hcp stacking sequence in the Ti layer.

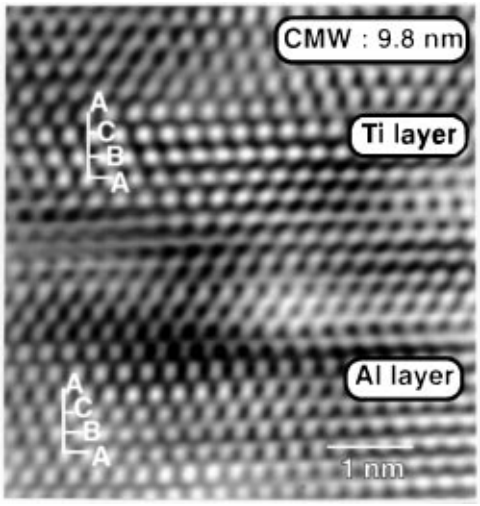

FIG. 3. HREM image from the cross section of the multilayer which has a bilayer thickness of 9.8 nm. The fcc stacking sequence existing in both the Al layer and the Ti layer is shown in the figure.

where μ_b is the bulk stacking fault energy, d is in units of the interplanar distance, ΔV_2 is the difference in the second nearest neighbor interaction between a faulted layer and an unfaulted one, E_F is the Fermi level, $B(E_F)$ is a slowly varying function of the band occupancy, V_1 is the nearest neighbor hopping integral, and δ is the phase shift. ΔF stands for a difference in the bandwidths, band fillings, interfacial bonding, or a combination of these [5]. The bicrystal interface introduces a Friedel-like oscillatory modulation of wavelength λ_F to the bulk stacking fault chemical potential. A metallic superlattice can be considered to be a system which consists of a sequence of bimetallic interfaces and the stacking sequence is determined by the resultant of the superposition of the primary bounding oscillatory potentials in each layer.

The Redfield-Zangwill model is applicable to metallic superlattices formed from two different close-packed metals with similar lattice parameters [5]. Bulk Ti and Al are hcp and fcc, respectively, and the interplanar distance of closed-packed planes in both metals differ by only 0.07%. Therefore, it would be appropriate to apply this model to Ti/Al superlattices where the effect of elastic distortions on the structural transitions occurring in these multilayers is not expected to be dominant. Furthermore, low angle x-ray diffraction (XRD) studies revealed that the interface fluctuation width in each multilayer was less than 0.3% of the bilayer thickness [7]. An interesting observation is that for Ti, at a layer thickness of $\approx$5 nm, the structure changes to fcc, whereas for layer thicknesses $\approx$2.5 nm, the structure reverts to hcp. It is of interest to determine whether the Redfield-Zangwill model can predict such a behavior.

As stated earlier, the stacking sequence in each layer of a metallic superlattice is determined by the superpo-

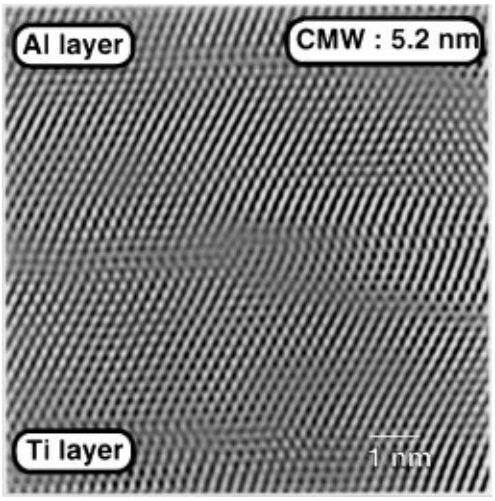

FIG. 4. HREM image from the cross section of the multilayer which has a bilayer thickness of 5.2 nm. It shows the hcp stacking sequence present in both the Ti and the Al layers.

sition of symmetrical Friedel-like oscillatory modulations of wavelength λ_F, arising from the bounding bicrystal interfaces. For simplicity, assume a linear superposition of these bounding modulations. Consequently, the net potential of stacking faults in a layer is determined by the phase difference between the two bounding modulations which in turn is a function of the layer thickness. Since the bounding modulations are basically damped sinusoidal waves, as the layer thickness reduces, the superposition of the modulations oscillates between constructive and destructive interference regimes. At large layer thickness values, much larger than the value of λ_F, the effect of superposition is not felt and the bulk crystal structures dominate; for example, this applies to the 108 nm multilayer. As the layer thickness is reduced to the extent that superposition effects contribute to the stacking sequence, constructive interference can result in certain regions of a layer having a negative net stacking fault potential and a positive value in other regions of the same layer. This leads to a mixed fcc + hcp structure within the same layer, such as is observed in the Ti layers of the 21 nm multilayer. It should be noted that the layer thickness is still greater than the wavelength λ_F, of the oscillatory modulations. Further reduction of the layer thickness below λ_F will initially result in a constructive interference such that the stacking fault potential is negative throughout the layer, converting an entire layer of hcp to fcc or vice versa [5]. This is observed in the Ti layer of the 9.8 nm multilayer and in the Al layer of the 5.2 nm multilayer suggesting that the λ_F for Ti is larger than that for Al. However, on further reduction of the layer thickness, the interference again becomes destructive, stabilizing the bulk crystal structure in the layer; this is observed in the Ti layers of the 5.2 nm multilayer. It appears from the above discussion that the Redfield-Zangwill model is able to predict, in principle, a sequence of transformations in a multilayer with reducing layer thickness as follows:

$$\text{hcp} \rightarrow \text{fcc} + \text{hcp} \rightarrow \text{fcc} \rightarrow \text{hcp}$$

or

$$\text{fcc} \rightarrow \text{hcp} + \text{fcc} \rightarrow \text{hcp} \rightarrow \text{fcc}\,.$$

From the discussion given above it is clear that the critical quantity in Eq. (1) is the Friedel oscillatory wavelength, and, therefore, it would be more satisfactory if a more quantitative approximation of λ_F were to be deduced, which would lend credibility to the model. This is done by deriving an expression for λ_F from Eq. (1) as follows:

$$\lambda_F = \pi/\cos^{-1}[(E_F/6V_1) + 1], \qquad (2)$$

where λ_F is in units of the interplanar distance. Since a first principles computation of the nearest neighbor hopping integrals and Fermi levels is beyond the scope of this paper, an approximate estimate of these quantities has been made on the basis of a linear combination of atomic orbitals (LCAO) using the Slater-Koster (SK) method as an interpolation scheme [8]. The Redfield-Zangwill model assumes the simplest possible tight binding model of the metals with one s site per atom with site energy E [5]. Consequently, the only energy integral of interest is $V_{ss\sigma}$. The computed values of $V_{ss\sigma}$ for bulk Ti and Al are $V_{ss\sigma}(\text{Ti}) = -0.5182$ Ry and $V_{ss\sigma}(\text{Al}) = -0.5153$ Ry. The corresponding Fermi energy values are $E_F(\text{Ti}) = 0.1392$ Ry and $E_F(\text{Al}) = 0.1637$ Ry. As a first approximation, the Fermi energy level of the multilayered structure as a whole has been assumed to be midway in between the

TABLE I. Table showing the structural parameters of the four different Ti/Al multilayers, having a range of bilayer thickness values, which have been investigated in the present study.

Bilayer Thickness (nm)	Ti structure	Al structure	Ti d-spacing (nm)	Al d-spacing (nm)
108	hcp	fcc	{0002} = 0.2316	{111} = 0.2333
21	hcp + fcc	fcc	{0002} = 0.2244 {111} = 0.2485	{111} = 0.2296
9.8	fcc	fcc	{111} = 0.2501	{111} = 0.2296
5.2	hcp	hcp	{0002} = 0.2314	{0002} = 0.2314

Fermi levels of bulk Ti and Al giving $E_F = 0.1515$ Ry. The values of V_1 have been calculated by a process of normalization which involves multiplying the values of $V_{ss\sigma}$ by the number of valence electrons for both Ti and Al given by $V_1(\mathrm{Ti}) = 4V_{ss\sigma}(\mathrm{Ti}) = -2.0728$ Ry and $V_1(\mathrm{Al}) = 3V_{ss\sigma}(\mathrm{Al}) = -1.5459$ Ry. Substituting these values in Eq. (2), $\lambda_F(\mathrm{Ti}) = 20$ and $\lambda_F(\mathrm{Al}) = 17$ (in units of the relevant interplanar spacing) have been determined.

From the experimental observations, it can be concluded that the total transformation of the Ti layers from an hcp structure to an fcc structure occurs in the range of layer thickness of 10.5 to 4.9 nm, corresponding to a range of 45 to 20 close-packed atomic layers. This range is on the higher side of the theoretically calculated value of 20 atomic layers for λ_F of Ti, although it is a reasonably good first approximation. In the case of Al, the theoretically predicted value of $\lambda_F = 17$ lies within the experimentally determined range of 21 to 11 close-packed atomic planes. On the basis of this agreement it seems that the Redfield-Zangwill model can make reasonable order of magnitude predictions about the layer thickness at which fcc $\leftrightarrow$ hcp type of structural transitions occur in metallic multilayers. Another predication of this model [5] is the possibility of the occurrence of ordered sequences of stacking faults in the layers of a metallic superlattice leading to the formation of long period polytype structures such as those which have been observed in Ru-Ir superlattices [1]. However, no such ordered sequence of stacking faults was observed in any of the Ti/Al multilayers investigated.

An additional point to be considered is the difference in the value of μ_b for Ti and Al, which decides the extent of shift of the bounding modulation in the positive sense. The values of μ_b for Ti [9] and Al [10] are 30 and 135 $\mathrm{mJ/m^2}$, respectively. Since the bulk stacking fault potential for Al is much greater than that for Ti, the modulations in the Al layers are shifted to a larger extent in the positive sense. Consequently, the region of negative potential in the bounding modulations is confined nearer to the interface in the Al layers as compared to the Ti layers. So the net potential in the Al layers falls below zero only for a smaller layer thickness when the superposition of modulations close to the interface region is in effect.

In this Letter a series of novel structural transitions occurring in Ti/Al multilayered thin films, dependent on the bilayer thickness of the multilayers has been discussed. It is evident from the experimental results that the stability of the competing closed packed crystal structures, hcp and fcc, is a strong function of the layer thickness which imposes a dimensional constraint. A possible explanation for the structural transformations occurring in these multilayers has been proposed based on the Redfield-Zangwill model. However, a comprehensive model would need to account for other factors, for example, elastic distortions, and this complex problem is the subject of future research.

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