Comparison of size dependent strengthening mechanisms in Ag/Fe and Ag/Ni multilayers

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Abstract:

Nanostructured metallic multilayers have attracted substantial attention as they often possess high mechanical strength. Here we report on the microstructure and mechanical strength of sputtered Ag/Fe multilayers with individual layer thicknesses (h) varying from 1 to 200 nm. Phase transformation of Fe from body-centered-cubic (bcc) to face-centered-cubic (fcc) structure occurred when $h < 5$ nm. Nanotwins formed in fine Ag/Fe multilayers. Although modulus mismatch is similar between Ag/Fe and Ag/Ni multilayers, the peak hardnesses of Ag/Fe multilayers is much lower than that of Ag/Ni system. Comparison of mechanical strength of several Ag based multilayers reveals that this drastic difference may arise from chemical stress due to the difference in stacking fault energy of the layer constituents.

Keywords: sputter; multilayer; strengthening; nanoindentation; stacking fault energy

1. Introduction

Nanostructured metallic multilayers (NMMs) have advanced physical properties and have been widely studied for various applications, including magnetic data storage [1, 2], hydrogen storage [3, 4], and radiation tolerance [5-13] etc. In addition, NMMs may have applications as the future micro/nano-electromechanical devices as certain multilayer systems exhibit close to theoretical strength and relatively large deformability [14-18]. Size-dependent strengthening in NMMs, that is the evolution of film hardness as a function of individual layer thickness, h , has been extensively studied [16, 19-28].

Since the establishment of the Hall-Petch (H-P) model in 1950th, it has been widely adopted to explain the grain boundary (GB) induced strengthening mechanism due to dislocation pile-ups [29, 30]. The H-P model also works well for NMMs [10, 15, 16, 24, 31-37] when the individual layer thickness h is greater than tens of nanometers (normally when $h > 50$ nm). At this length scale, the hardness increases linearly with $h^{-1/2}$, and the H-P slope has been used to estimate the interface barrier strength and predict the peak hardness of multilayers. However, if the multilayers contain a significant number of defects, such as nanotwins and nanograins, that have much smaller dimensions than h , the peak hardness predicted from the H-P slope may show a substantial deviation from the measured values [15, 34, 36-40].

When h decreases to below 50 nm, film hardness deviates from the linear prediction of the H-P model, as dislocation pile-ups are less likely at such a small length scale. Instead, the confined layer slip (CLS) model derived from the Orowan bowing of single dislocations may be a more realistic deformation mechanism [18, 22]. At this length scale, dislocation movement is confined within the layers since the stress required for transmission of dislocations across interfaces is larger than that to bow dislocations in form of hairpins. A refined CLS model has also been developed by taking interface stresses and misfit dislocations into account, and the model describes the size dependent hardness evolution of certain metallic multilayers fairly well [24, 36].

When h reduces to several nm (generally 1 ~ 5 nm), the strength of NMMs typically reaches a plateau and is independent of h . The maximum (or plateau) strength of the multilayers is determined by various mechanisms, including Koehler stress [41-43], misfit dislocations [15, 36, 42, 44], chemical stress [3, 15, 35, 42], coherency stress [42, 45] and twinning [33, 35-37,

46]. A hardness plateau is generally observed at smaller h in incoherent systems [16, 17, 30, 34, 47], while softening often occurs in coherent systems due to the formation of fully coherent interfaces (also referred to as transparent interfaces, that is the interface is transparent to the transmission of dislocations) [16, 32, 42].

A substantial number of prior studies have focused on the microstructural evolution and mechanical properties of NMMs with various types of interfaces, including fcc/fcc [15, 31, 35, 37], bcc/bcc [37, 48, 49], hcp/hcp [50], fcc/bcc [16, 17, 23, 36], fcc/hcp [33, 40] and bcc/hcp [51-53] interface (fcc: face-centered cubic; bcc: body-centered cubic; hcp: hexagonal close-packed). Among these systems, fcc/bcc multilayers with opaque and immiscible layer interfaces have attracted considerable attention as such interfaces are strong barriers to the transmission of dislocations because of the discontinuity of slip systems [54, 55]. Cu/Nb, Cu/V and Cu/Fe are some of the typical multilayers with fcc/bcc interfaces [16, 56]. Molecular dynamics (MD) simulations have shown that the interfaces in Cu/Nb multilayer systems exhibit lower elastic modulus than layer constituents and thus the stress field of a glide dislocation can locally shear the interface and lead to dislocation core spreading along “weak” layer interfaces. The reemission of dislocations therefore becomes very difficult [55]. The study on Cu/V showed that weak interface and slip discontinuity may be the key to determining the peak strength in this system [17]. The strengthening mechanism in Cu/Fe system is slightly different, as high strength is observed in multilayers with relative large h (50 ~ 100 nm). The high strength over this length scale is ascribed to the confined dislocation propagation within nanoscale columnar grains (in the Fe layers), which are much smaller than h [36]. High-density growth twins have been observed in fully coherent (111) Cu/Fe multilayers when $h = 0.75$ nm and Fe has transformed to fcc structure. Peak hardness was retained because nanotwins are strong barrier to the transmission of dislocations [57, 58]. In Ag/V system, multiple growth orientation relations, including K-S, N-W, Bain as well as other intermediate relations, exist between two layer components, and therefore the habit planes change locally with the curvature of the interfaces [59].

Nanotwins have been extensively observed in some fcc/fcc multilayer systems, such as Cu/Ni [37], (100) textured Cu/Co ((100) Co has fcc phase) [33], Ag/Al [35], Ag/Ni [15], etc., and twin boundaries (TBs) contribute significantly to their peak strength. For instance, in (111) textured Cu/Ni multilayers, nanotwins significantly enhance the mechanical strength compared

with their (100) textured counterparts. However, the large difference in peak hardness between (100) Cu/Ni and (100) Cu/Co (Co has transformed to fcc phase) is unexpected as both systems have nearly epitaxial microstructure, similar lattice mismatch ($\sim 2.6\%$) and elastic modulus mismatch. Such a large difference in hardness has led to a hypothesis that the difference in stacking fault energy (SFE) between layer constituents could contribute significantly to the strength of multilayer systems [33].

In this study, we selected Ag/Fe multilayers for the following reasons. First, the strengthening mechanisms in Ag/Fe with fcc/bcc interfaces are less well understood. Prior studies on Ag/Fe focused on their magnetic properties [60], microstructures and indentation creep behavior [61-63]. Second, when comparing Ag/Fe and Ag/Ni, it is evident that the elastic modulus of Fe and Ni are similar. Thus the Koehler stress due to elastic modulus difference should be similar in both Ag/Fe and Ag/Ni multilayers. Consequently, we anticipate that Ag/Fe and Ag/Ni multilayers should have comparable peak strength. Such a hypothesis will be tested. Third, we will compare the mechanical strength of Ag/Fe to Cu/Fe multilayers. In Cu/Fe multilayers, the grain size of Fe is smaller than h and determines the mechanical strength of system at large h ($h > 50$ nm). At small h (1 nm or so), Cu and Fe form coherent interfaces as Fe has transformed to fcc phase. Softening has been observed in Cu/Fe with small h due to the formation of coherent (transparent) interfaces. Furthermore, nanotwins with an average twin spacing of ~ 6 nm has been observed in Cu/Fe multilayers. It is unclear if twins can form in Ag/Fe multilayers at this small length scale; and if softening exists in Ag/Fe multilayers.

In this paper, we provide a comprehensive study on the microstructures of Ag/Fe multilayers by transmission electron microscopy (TEM), and the mechanical properties of Ag/Fe multilayers obtained by nanoindentation. The comparison of size dependent strengthening mechanisms in Ag/Fe to other systems, such as Ag/Ni and Cu/Fe, reveals several surprises, and the conclusion derived from this study may have general implications on size dependent strengthening mechanisms in numerous metallic multilayer systems.

2. Experimental

Ag/Fe multilayer thin films with identical individual thicknesses, h , varying from 1 to 200 nm and overall thicknesses of 1-4 μm were deposited onto HF acid etched single crystal Si (111) substrates via DC magnetron sputtering at room temperature from pure Ag (99.99%) and Fe (99.95%) targets. A base pressure of better than 8×10^{-8} torr was achieved before deposition, and the Ar pressure during deposition was 2~3 mtorr. A 50 nm-thick Ag buffer layer was deposited before the deposition of any Ag/Fe multilayers. The indentation hardness was measured using a Fischerscope HM2000XYp micro/nanoindenter with a Vickers indenter tip using instrumented nanoindentation technique. Approximately 15 indents were performed at different locations with different indentation depths. Each indent will typically penetrate into several bilayers, and the maximum depth was kept to be less than 15% of total film thickness to avoid the substrate effect. Hardness versus indentation depth was plotted, and the plateau value was chosen as the hardness of the measured film. X-ray diffraction (XRD) experiments were performed by using a PANalytical X'Pert PRO Materials Research Diffractometer (Cu $K\alpha$ radiation) at room temperature. Transmission electron microscopy (TEM) studies were carried out on both FEI Tecnai F20 Super Twin microscope and JEOL 2010 TEM microscope operated at 200 kV. Cross-sectional TEM (XTEM) samples were ground and polished mechanically, and further thinned by dimpling. Finally, low energy Ar ion milling (3.0~4.0keV) and ion polishing (2.0 keV) were involved in reducing film thickness to roughly 100 nm.

3. Results

3.1. Microstructure characterization

Fig. 1a compiles XRD profiles of as-deposited Ag/Fe multilayers on Si (111) substrates. When $h > 50$ nm, Fe layers had bcc (110) texture, while Ag layers had strong (111) texture. The Fe (110) peak shifted to lower angles when $h < 25$ nm. The magnified XRD patterns for multilayers with h of 1 ~ 10 nm in Fig. 1b show a peak with interplanar distance of $\frac{1}{2} (d_{\text{Ag}}^{(111)} + d_{\text{Fe}}^{(111)})$ and a Ag (111) superlattice satellite peak ($n = +1$) in the Ag 5 nm/Fe 5 nm (referred to as Ag/Fe 5 nm) multilayer. Additionally, fcc Fe (111) peak emerged in Ag/Fe 5 nm and Ag/Fe 2.5 nm multilayers. The Ag/Fe 1 nm multilayer exhibited a single predominant Ag (111) peak, indicating the formation of strong (111) texture.

A bright-field XTEM micrograph and the corresponding selected area diffraction (SAD) patterns of Ag/Fe 200 nm multilayer are shown in Fig. 2a and 2b respectively. The SAD pattern indicates the formation of polycrystalline film with strong bcc Fe (110) and Ag (111) texture. Furthermore, Fe layers had nanoscale columnar grains with an average grain size of ~ 21 nm, much smaller than that (~ 106 nm) in Ag layers as shown in Fig. 2c. The average columnar grain size clearly evolved with h , as shown in Fig. 2d. When $h > 50$ nm the average columnar grain size of Ag decreased from 106 ± 25 to 28 ± 6 nm, and the grain size of Fe decreased from 21 ± 5 to 9 ± 4 nm. When h decreased to below 50 nm the grain size of Ag and Fe did not decrease further.

Fig. 3a shows clear layer interfaces in the Ag/Fe 5 nm multilayers deposited on Si (111) substrates. The SAD pattern of Ag/Fe 5 nm multilayer (in Fig. 3c) examined from the Ag $\langle 110 \rangle$ zone axis reveals the following orientation relationship: $(111)_{\text{Ag}} // (110)_{\text{Fe}}$, $[110]_{\text{Ag}} // [100]_{\text{Fe}}$, that is the typical N-W orientation. Also we have observed twinned orientation among Ag diffraction spots (as shown by the green and blue dotted lines). The SAD pattern of the Ag/Fe 5 nm multilayer examined from an orthogonal direction (along the Ag $\langle 112 \rangle$ zone axis) shows that $(111)_{\text{Ag}} // (110)_{\text{Fe}}$, $[112]_{\text{Ag}} // [110]_{\text{Fe}}$. Fig. 3b shows schematically the orientation relationship between Ag and Fe in the Ag/Fe 5 nm multilayer.

Fig. 4 and Fig. 5 show separately, the existence of both incoherent and coherent interfaces in Ag/Fe 5 nm multilayer on Si (111) substrate. High-resolution TEM (HRTEM) micrograph in Fig. 4a shows distinct layer interfaces between Ag and Fe. Fast Fourier transform (FFT) and the corresponding inverse FFT (IFFT) in the selected areas in Ag and Fe layer as well as along their interface are shown in Fig. 4b1 – b3 respectively. Ag is examined from $\langle 110 \rangle$ zone axis, and Fe has bcc phase along $\langle 100 \rangle$ zone axis. Fig. 4b3 shows a clear incoherent interface between fcc Ag and bcc Fe. In contrast, the HRTEM micrograph in Fig. 5a shows the formation of coherent interfaces in the same Ag/Fe 5 nm multilayer specimen. Three interfacial zones (labeled as A, B and C in Fig. 5a) are examined in detail. The magnified HRTEM micrograph in Fig. 5b2 shows a nearly coherent Ag/Fe interface formed at location B, and Fe had distorted fcc structure. Furthermore, an interesting hetero-twinning relationship is evident between Ag and Fe. As shown in Fig. 5b1 and Fig. 5b3, TBs formed between the adjacent Ag and

fcc Fe layers. The zigzag pattern of these plane traces in the schematic in Fig. 5a clearly shows the twin orientation relationships between successive layers.

Interface coherency was further enhanced when $h < 5$ nm. For instance the HRTEM micrographs of Ag/Fe 2.5 nm multilayer in Fig. 6a and the magnified TEM micrographs of the box d (Fig. 6c and 6d) show the formation of nearly coherent Ag/Fe interfaces. Although coherent interfaces are frequently observed in this specimen, the SAD pattern in Fig. 6b shows the existence of distorted fcc Fe. **In particular the 6 {111} fcc Fe diffraction spots appear to match the diffraction pattern of the Ag <110> zone axis.** Similar to Fig. 6, several HRTEM micrographs of the Ag/Fe 1 nm film in Fig. 7a, 7c and 7d confirm the formation of semi-coherent interfaces with distorted fcc Fe. The SAD pattern in Fig. 7b shows the formation of distorted fcc Fe examined along <110> zone axis. Furthermore the HRTEM micrograph in Fig. 7d shows a stacking fault in Fe and a misfit dislocation at the Ag/Fe layer interface.

3.2 Multilayer hardness

The hardnesses of Ag/Fe multilayer films on Si (111) substrate as a function of $h^{-1/2}$ are compared with Cu/Fe (111) [36] and Ag/Ni (111) multilayers [15] in Fig. 8. The peak hardness of Ag/Ni is ~ 6 GPa (when $h = 1$ nm), comparing to ~ 4 GPa for the Ag/Fe 5 nm multilayers and ~ 4.5 GPa for the Cu/Fe 1 nm multilayers. Three distinct characteristics are noteworthy in this plot:

- (1) When $h \geq 50$ nm, the hardnesses of Cu/Fe and Ag/Fe are larger than Ag/Ni. In addition, the H-P slope is $\sim 4.5 \text{ GPa} \cdot \text{nm}^{1/2}$ for Ag/Fe multilayers, much smaller compared with that for the Cu/Fe multilayers, $\sim 10.3 \text{ GPa} \cdot \text{nm}^{1/2}$, and Ag/Ni, $\sim 19.8 \text{ GPa} \cdot \text{nm}^{1/2}$.
- (2) When $50 \text{ nm} > h \geq 5$ nm, Ag/Ni multilayers become harder than Ag/Fe, but remain softer than Cu/Fe multilayers.
- (3) When $h < 5$ nm, the hardness of Ag/Ni continuously increases and finally becomes larger than that of the Ag/Fe and Cu/Fe films. No softening is observed for the Ag/Ni and Cu/Fe systems while softening occurred in the Ag/Fe multilayers.

4. Discussion

4.1 Microstructure evolution of Ag/Fe multilayers

4.1.1 Coherency and phase transformation of Fe when $h \leq 2.5$ nm

Our previous study on Cu/Fe multilayers showed clear h dependence of columnar grain size in both Fe and Cu layers [36]. A similar phenomenon has been observed in this study. When $h = 200$ nm, the grain size of Ag is ~ 106 nm, which is approximately five times that of Fe (~ 21 nm). The lattice constants of Ag and bcc Fe are $4.085 \text{ \AA}$ and $2.867 \text{ \AA}$, respectively. Thus in general, Ag and Fe should form incoherent interfaces due to the large lattice mismatch, $\sim 35\%$. However, a middle peak and a superlattice peak were observed when $h = 5$ and 2.5 nm. Furthermore, the Fe (110) peak gradually shifted to smaller 2θ angle and finally diminished at $h = 1$ nm. These observations indicate that semi-coherent interfaces might have formed when $h < 10$ nm. More specifically when $h = 1$ nm, coherent interface may have become dominant as implied by the single predominant Ag (111) peak in XRD pattern. Meanwhile, Fe might experience a bcc-to-fcc phase transformation (as evidenced by the HRTEM micrographs in Fig. 7). The formation of semi-coherent Ag/Fe interfaces with distorted fcc Fe phase is somewhat surprising. Coherent Cu/Fe interfaces have been observed before, where fcc Fe has lattice parameters, $\sim 3.585 \text{ \AA}$, similar to that of Cu ($3.615 \text{ \AA}$).

The critical film thickness to keep coherent interface (free from misfit dislocation) can be estimated by [64],

$$h_c = \frac{b}{8\pi(1+\nu)\varepsilon_m} \left[\ln \left(\frac{h_c}{b} \right) + 1 \right] \quad (1),$$

where h_c is often referred to as the critical layer thickness for the formation of misfit dislocations, the magnitude of the Burgers vector b is ~ 0.25 nm, the mismatch strain ε_m between Ag and fcc Fe is 13% , and the Poisson's ratio ν is 0.33 . The calculated value for h_c is ~ 0.5 nm. In Ag/Fe multilayers, since Fe is sandwiched by two Ag layers, the maximum thickness for maintaining coherent interface could be $2h_c = \sim 1$ nm. Thus, it is feasible that Ag/Fe may exhibit semi-coherent interface when $h = 1$ nm.

When $h = 2.5$ nm, we also observed coherent Ag/Fe interface (as revealed by TEM micrographs in Fig. 6). Additionally, the same multilayer also shows the formation of distorted bcc Fe, as indicated by the SAD pattern in Fig. 6b. **It appears that 6 fcc Fe {111} diffraction**

spots tend to match the diffraction spots of fcc Ag (along <110> zone axis). Such an intriguing phenomenon has not been reported before.

4.1.2 Hetero-twin formation when $h = 5$ nm

Although fcc Fe could form in Ag/Fe 1 nm multilayers, the formation of fcc Fe in Ag/Fe 5 nm multilayers is even more surprising. Both semi-coherent Ag/Fe (fcc Fe) and incoherent Ag/Fe (bcc Fe) interfaces were observed in Ag/Fe 5 nm multilayers. Furthermore, we have observed hetero-twins formed between Ag and Fe, that is the Ag/Fe layer interface may also serve as a TB between the two constituents in the Ag/Fe 5 nm multilayer. A somewhat similar observation has been reported in a metal/ceramic system, Al/TiN, where alternating Al layers may have a twin orientation separated by adjacent TiN layers [65]. Nanotwins have been observed in Cu/Fe 0.75 nm multilayers, and the average twin spacing is typically 6 nm [36]. In the current study, however, nanotwins were barely observed in Ag/Fe 1nm multilayers.

4.2 Strengthening mechanisms in Ag/Fe multilayers and comparisons to other systems

4.2.1 Strengthening at large layer thickness where $h = 50 - 200$ nm

Previous studies typically show that, when $h > 50$ nm, the hardness of multilayer films scales approximately linearly with $h^{-1/2}$. The maximum hardness can be estimated reasonably well by using a traditional H-P relationship [29, 30, 66]:

$$H_{IT} = H_0 + k_{HP}h^{-0.5}, \quad (2)$$

where H_0 is the hardness when the grain size is infinitely large and it represents the overall resistance of the crystal lattice to dislocation motion. H-P slope, k_{HP} , is a measure of the relative hardening contribution from layer interfaces, and can be expressed via [66]:

$$k_{HP} = \sqrt{\tau^*Gb/[\pi(1 - \nu)]} \quad (3),$$

where τ^* is the interface barrier strength, G is the shear modulus (30 GPa for Ag), b is 0.289 nm for Ag, and ν is ~ 0.33 . From k_{HP} measured from the H_{IT} vs. $h^{-1/2}$ plot, 4.45 GPa·nm^{1/2}, we calculate τ^* to be 0.073 GPa. The Tabor relation, $H = 2.7\sigma$, can be used to estimate peak hardness [67], where σ is the flow stress and can be calculated by taking into account the Taylor factor so that $\sigma = 3\tau^*$. Thereby the peak hardness ($=8.1\tau^*$) is estimated to be ~ 0.6 GPa, which is

much lower than the measured value, ~ 4.4 GPa. Thus the measured H-P slope in the current study cannot predict the peak hardness of Ag/Fe multilayer films, different from numerous prior studies [15, 17, 31, 33]. When comparing Ag/Fe to Cu/Fe multilayers, it is evident that the Cu/Fe multilayers have similarly low H-P slope [36]. Furthermore when $h > 50$ nm, the hardnesses of Ag/Fe and Cu/Fe multilayers are much greater than that of Ag/Ni with identical h . This is primarily because the Fe layers have small columnar grain sizes, ~ 20 nm, much smaller than h . In this case, the deterministic dimension for film hardness is no longer h , but columnar grain size. Thus once dislocations (nucleated in Ag layers) propagate through Ag/Fe layer interfaces, they will be confined by the narrow columnar grain boundaries (channels) in Fe. In this case the stress for the propagation of dislocations (via Orowan bowing) in Fe layers may determine the hardness of Ag/Fe multilayers over this length scale ($h > 50$ nm). In contrast, the columnar grain sizes in Ag/Ni multilayers are comparable to layer thickness, and thus the strength of Ag/Ni multilayers is lower than that of Ag/Fe multilayers.

4.2.2 Strengthening mechanisms when $h = 25 - 10$ nm

At these length scales, the hardness is no longer dominated by columnar grain boundaries because their dimension is comparable or greater than individual layer thickness (refer to Fig. 2d). Consequently, dislocation pile-ups become less effective, and the movement of single dislocations is confined within the layers and the strengthening mechanism is described by the CLS model based on Orowan bowing mechanism. The critical resolved shear stress τ_{CLS} needed to initiate dislocation movement can be calculated as [18, 22]:

$$\tau_{CLS} = \frac{Gb}{8\pi h'} \left(\frac{4-\nu}{1-\nu} \right) \left(\ln \frac{h'}{b} \right) \quad (4),$$

where h' is the effective layer thickness - the distance along the slip plane between adjacent interfaces. Other variables carry the same meaning as defined previously. Using $G_{Ag} = 30$ GPa, $b_{Ag} = 0.289$ nm, $\nu = 0.33$ and $h' = \sqrt{2}h = 14$ nm (corresponding to $h = 10$ nm), the τ_{CLS} is calculated to be ~ 0.52 GPa, corresponding to a hardness value of ~ 4.2 GPa. This is in agreement with the measured hardness value of ~ 4.0 GPa. The size dependent strengthening in Ag/Ni multilayers in this regime has similar trend comparing to Ag/Fe. Furthermore, the hardnesses of the two systems over this length scale are very close at the same h .

4.2.3 Peak hardness when $h = 5$ nm

The hardness of Ag/Ni multilayers reaches a maximum value of ~ 4.4 GPa when $h = 5$ nm. At such a length scale, the maximum strength is determined by the intrinsic resistance of the Ag/Fe interface to the transmission of dislocations. In general, the interface barrier strength, $\tau_{barrier}$ can be estimated by [68]:

$$\tau_{barrier} = \tau_k + \tau_d + \tau_{ch} \quad (5),$$

The first term τ_k is the Koehler stress due to the difference in elastic modulus of the layer constituents. The maximum τ_k can be estimated by [41]:

$$\tau_k = R G_{Ag} \sin \theta / 8\pi \quad (6),$$

where $R = (G_{Fe} - G_{Ag}) / (G_{Fe} + G_{Ag})$, G_{Fe} and G_{Ag} are the shear moduli of Fe and Ag separately. θ is the angle between the slip plane and the interface. Assuming $\theta = 54.74^\circ$, the Koehler stress τ_k is calculated to be ~ 0.44 GPa, corresponding to a hardness of ~ 3.6 GPa.

The second term τ_d arises from misfit dislocations, and the third term τ_{ch} originates from the difference in SFE of each layer constituent. Since fcc Ag and bcc Fe have incoherent interface, the contribution of misfit dislocations to hardness is negligible. Therefore, the maximum hardness in Ag/Fe system is mainly dominated by Koehler stress. Hardness of the Ag/Fe multilayers at such length scale could also be related to hetero-twinned structure between adjacent Ag and Fe layers. TBs form at the Ag/Fe interfaces. It has been shown previously by both experiments and molecular dynamics simulations that TBs are strong barriers for the transmission of dislocations[57, 69]

4.2.4 Softening when $h = 2.5 - 1$ nm

When individual layers become extremely thin (1-2.5 nm in thickness), the hardness decreases with decreasing h due to the increase of interface coherency. Coherent and semi-coherent interfaces have lower resistance than incoherent interfaces to the transmission of dislocations. Hence such interfaces are sometimes referred to as more “transparent” interfaces to dislocations than incoherent (also called “opaque”) interfaces [54, 55]. The softening in coherent and semi-coherent multilayers at small h is also related to the decreasing Koehler stress as the dislocation core radius is comparable to layer thickness [42]. A similar result has been observed

in Cu/Fe (100) [36] and Cu/Ni (100) multilayers [37]. However, no or little softening occurs in the coherent (111) Cu/Fe 1nm and (111) Cu/Ni 2.5 nm multilayers due to the formation of high-density growth twins.

4.3 The role of stacking fault energy in the determination of peak hardness

The interface barrier strength, in general, determines the maximum strength of multilayers. Some factors, such as τ_k , τ_d and chemical stress τ_{ch} are taken into account to estimate the total interface strength. Among these factors, τ_k and τ_d have been widely investigated. In contrast, the contribution from chemical stress τ_{ch} are less well understood. To better understand the role of SFE in the determination of multilayer peak hardness, all three terms (τ_k , τ_d and τ_{ch}) for several systems, Ag/Fe, Ag/Ni, Cu/Fe and Ag/Al are compared in Table 2, and Table 1 lists the shear modulus, SFE and lattice type and constant for these systems.

It is not surprising to see that Ag/Fe and Cu/Fe have the similar peak hardness since in both systems, τ_k is the primary term and similar for Ag/Fe and Cu/Fe multilayers. Whereas it is unexpected that Ag/Ni is ~ 2 GPa harder than Ag/Fe because Koehler stress is exactly the same for these two systems. Such a big difference in peak hardness can be explained in terms of the chemical stress, τ_{ch} , which can be estimated by [41, 42]

$$\tau_{ch} = \frac{\gamma_{Ag} - \gamma_{Fe}}{b} \quad (7),$$

where τ_{ch} is chemical stress, γ_{Ag} and γ_{Fe} are respective SFE of Ag and Ni, and b is Burgers vector of Ag. In Ag/Ni, the SFE difference between Ag (10 mJ/m²) and Ni (110 mJ/m²) is very large, resulting in a large chemical stress term, ~ 0.3 GPa in Ag/Ni; while the chemical stress is negligible in Ag/fcc Fe (as fcc Fe also has very low SFE, ~ 20 mJ/m² [70]). Another interesting comparison is made between Ag/Fe and Ag/Al multilayers, where Ag/Al is more than 1 GPa harder than Ag/Fe multilayers. The Koehler stress in Ag/Al, is roughly an order of magnitude smaller than Ag/Fe (0.05 GPa vs. 0.44 GPa), but the chemical stress τ_{ch} for Ag/Al is significant, ~ 0.5 GPa, due to the giant SFE difference between Ag and Al (10 mJ/m² vs. 180 mJ/m²). Consequently the Ag/Al multilayers have higher peak hardness than Ag/Fe multilayers [35].

The difference in SFE may determine the peak hardness of multilayers with fcc/fcc interfaces to a greater extent. Our recent studies show that the peak hardness of (100) textured Cu/fcc Co is much smaller than that of (100) Cu/Ni multilayers [33]. When Co transforms to fcc phase (in (100) Cu/Co multilayers), the chemical stress is very low as both Cu and fcc Co have low SFE. Consequently, the partial dislocations nucleated in fcc Cu may transmit across the Cu/fcc Co interface with low resistance. In contrast, the Cu/Ni system has a large SFE mismatch so that partials in Cu may have to constrict to perfect dislocations before they can transmit across the Cu/Ni interfaces (as Ni has a much greater SFE than Cu).

Comparison of normalized peak hardness ($H_{\text{peak}}/G_{\text{ave}}$) as a function of SFE difference $\Delta\gamma_{\text{SFE}}$ between two components in different Ag and Cu based multilayer systems (with fcc/fcc interfaces) is shown in Fig. 9. The dashed line shows a simple linear fit to the literature data. A clear trend is identified, that is $H_{\text{peak}}/G_{\text{ave}}$ increases with increasing $\Delta\gamma_{\text{SFE}}$, indicating that chemical stress may play a major role in determining the peak strength of a variety of Ag and Cu based multilayer systems. Such an observation may provide a fresh perspective for the design of high strength metallic multilayers.

5. Conclusions

Ag/Fe multilayers with various individual layer thicknesses were deposited on Si (111) substrate by magnetron sputtering. The coherency between Ag and Fe increases with decreasing h . Nearly coherent interfaces form in Ag/Fe 1 nm multilayers. Phase transformation from bcc to fcc Fe occurred when $h < 5$ nm. Hetero-twinned interfaces were observed between adjacent Ag and Fe when $h = 5$ nm. Comparisons of hardness between Ag/Fe, Ag/Ni, Cu/Fe and Ag/Al reveal the significance of stacking fault energy of layer constituents in the determination of peak hardness of multilayers with fcc/fcc interfaces.

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Table captions:

Table 1. Comparison of modulus, SFE, Δ SFE (SFE difference between two components) and crystal structure for several multilayer systems.

Note: In Cu/Fe and Ag/Fe multilayers, Fe has become fcc phase when h is ~ 1 -5 nm

Table 2. Comparison of Koehler stress (τ_k), misfit dislocation induced barrier stress τ_d , chemical stress (τ_{ch}), calculated peak hardness (H_{cal}^{peak}) and experimentally measured peak hardness (H_{exp}^{peak}) for several multilayer systems.

Note: ($\tau_{total} = \tau_k + \tau_d + \tau_{ch}$; $H_{cal}^{peak} = 8.1\tau_{total}$)

* τ_{total} in Ag/Al also comes from ω interaction.

Figure captions:

Fig 1. (a) XRD patterns of Ag/Fe multilayers deposited on Si (111) substrates. When $h > 50$ nm, Fe exhibits bcc (110) texture, while Ag has strong (111) texture. When $h < 25$ nm, the bcc Fe (110) peak shifts to lower angles. (b) Magnified XRD patterns for a multilayer with h of 1 ~ 10 nm. When $h = 5$ nm, a superlattice peak with $\frac{1}{2}(d_{Ag}^{(111)} + d_{Fe}^{(111)})$ forms, and both bcc Fe (110) and fcc Fe (111) peaks emerges. A Ag (111) satellite peak ($n = +1$) appeared when $h = 2.5$ nm. The bcc Fe (110) peak disappears when $h = 1$ nm, and the Ag/Fe 1 nm multilayer exhibits single predominant Ag (111) peak.

Fig 2. (a) A bright field cross-section TEM (XTEM) micrograph of Ag/Fe 200 nm multilayer showing the formation of nanoscale columnar grains in Fe layers. (b) The corresponding selected area diffraction (SAD) pattern reveals bcc Fe (110) and Ag (111) texture. (c) The statistical studies show that the average columnar grain size is ~ 106 nm for Ag, and 21 nm for Fe. (d) The evolution of columnar grain size as a function of h . When $h > 50$ nm the average columnar grain

size of Ag decreased from 106 ± 25 to 28 ± 6 nm, and the grain size of Fe decreased from 21 ± 5 to 9 ± 4 nm. When h decreased to below 50 nm the grain size of Ag and Fe did not decrease further.

Fig 3. (a) A bright field XTEM micrograph of Ag/Fe 5 nm multilayer on Si (111) substrates. N-W orientation relationship, $(111)_{\text{Ag}} // (110)_{\text{Fe}}$, $[110]_{\text{Ag}} // [100]_{\text{Fe}}$, between Ag and Fe was schematically illustrated in (b), and was revealed in SAD pattern in (c) examined along Ag $\langle 110 \rangle$ and Fe $\langle 100 \rangle$ zone axis. Ag layers have twinned orientations. The N-W orientation relationship was further proved in SAD pattern in (d) where the image was taken from the Ag $\langle 112 \rangle$ and Fe $\langle 110 \rangle$ zone axis.

Fig 4. The formation of incoherent interfaces in Ag/Fe 5 nm multilayer film on Si (111) substrate. (a) An HRTEM micrograph shows the clear interface between Ag and Fe. (b1 - b3) Fast Fourier transforms (FFTs) and the corresponding inverse FFTs (IFFTs) in the selected areas in Ag and Fe layer as well as along their interface. Ag is examined from $\langle 110 \rangle$ zone axis, whereas Fe has bcc phase as revealed along $\langle 100 \rangle$ zone axis. (b3) FFT and IFFT showing the incoherent interface between fcc Ag and bcc Fe.

Fig 5. Coherent interface and growth twins in the Ag/Fe 5 nm multilayer film. (a) HRTEM micrograph of the multilayer combined with the FFT of each individual layer and schematics showing the formation of twin boundaries (TBs) in the multilayer. (b1 and b3) HRTEM micrographs and FFTs show the formation of nearly coherent TBs between Ag and Fe in multilayers at two different locations (A and C in Fig. 6a). (b2) A nearly coherent Ag/Fe interface forms in box B and Fe has distorted fcc structure.

Fig 6. (a) A cross-sectional HRTEM micrograph of Ag/Fe 2.5 nm multilayer on Si (111) substrate. (b) The corresponding SAD pattern shows a largely distorted fcc Fe pattern, where the $\{111\}$ fcc Fe diffraction spots appear to match the diffraction spots from fcc Ag $\{110\}$ diffraction zone axis. (c-d) For the same specimen at a slightly different location, an HRTEM micrograph and the magnified box d at interface showing the formation of nearly coherent Ag/fcc Fe interface.

Fig. 7 (a) An HRTEM micrograph of Ag/Fe 1 nm film on Si (111) substrate. (b) The corresponding SAD pattern shows the formation of distorted fcc Fe examined along $\langle 110 \rangle$ zone axis. (c) The magnified view in box c showing nearly coherent Ag/Fe interfaces. (d) An inverse of FFT of the box d in Fig. 7a showing a stacking fault in fcc Fe and a misfit dislocation at the Ag/Fe layer interface.

Fig. 8. Comparison of size dependent hardnesses among Ag/Fe, Cu/Fe and Ag/Ni multilayers. No softening was observed in Ag/Ni, while both Ag/Fe and Cu/Fe show softening at small h . The peak hardness of Ag/Ni is ~ 6 GPa (when $h = 1$ nm), comparing to the peak hardness of ~ 4 GPa in Ag/Fe and ~ 4.5 GPa for the Cu/Fe multilayers (when $h = 5$ nm).

Fig. 9. Comparison of normalized peak hardness ($H_{\text{peak}}/G_{\text{ave}}$) as a function of stacking fault energy difference $\Delta\gamma_{\text{SFE}}$ between two components in different Ag and Cu based fcc/fcc multilayer systems. The dashed line shows a simple linear fit of the literature data. The values of $H_{\text{peak}}/G_{\text{ave}}$ appear to increase with increasing $\Delta\gamma_{\text{SFE}}$, indicating that chemical stress due to stacking fault energy difference plays a significant role in determining the peak strength of these multilayers.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1. Comparison of modulus, SFE, Δ SFE (SFE difference between two components) and crystal structure for several multilayer systems.

	Ag/Fe	Ag/Ni	Cu/Fe	Ag/Al
Shear modulus, G (GPa)	30/80	30/76	48/80	30/26
SFE (mJ m^{-2})	10/20	10/110	55/20	10/180
Δ SFE (mJ m^{-2})	10	100	35	170
Crystal structure	fcc/fcc	fcc/fcc	fcc/fcc	fcc/fcc
Lattice constant ($\text{\AA}$)	4.09/3.59	4.09/3.52	3.62/3.59	4.09/4.05

Note: In Cu/Fe and Ag/Fe multilayers, Fe has become fcc phase when h is $\sim 1\text{-}5$ nm

Table 2. Comparison of Koehler stress (τ_k), misfit dislocation τ_d , chemical stress (τ_{ch}), calculated peak hardness (H_{cal}^{peak}) and experimentally measured peak hardness (H_{exp}^{peak}) for several multilayer systems.

	τ_k (GPa)	τ_d (GPa)	τ_{ch} (GPa)	τ_{total}	H_{cal}^{peak}	H_{exp}^{peak}
Ag/Fe	0.44	0.09	-	0.53	4.3	4.3
Ag/Ni	0.44	-	0.31	0.75	6.1	6.0
Cu/Fe	0.37	0.25	-	0.62	5.0	4.8
Ag/Al	0.05	-	0.5	0.65*	5.3	5.5

Note: ($\tau_{total} = \tau_k + \tau_d + \tau_{ch}$; $H_{cal}^{peak} = 8.1\tau_{total}$)

* τ_{total} in Ag/Al also comes from ω interaction.