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SUPERHARDNESS EFFECT IN Au/Ni MULTILAYERS

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Superhardness Effect in Au/Ni Multilayers

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ABSTRACT

The presence of an enhanced hardness, that is a 'Superhardness Effect', is found as a behavior parallel to the Supermodulus Effect in Au/Ni multilayer structures. The submicron thick Au/Ni coatings are prepared by magnetron sputter deposition. A microindenter is used to measure load as a function of indentation depth. An increase in hardness is measured as the Au/Ni layer pair spacing decreases. A local maximum in hardness occurs for samples with layer pairs consisting of 4-6 atomic planes of each metal component.

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I. INTRODUCTION

The Supermodulus Effect is a several-fold increase, beyond a rule-of-mixtures value, in the elastic constants of a metallic multilayer system. The increase in the in-plane elastic moduli, as measured using a variety of mechanical tests^[1-4] and acoustic wave methods^[5], are found over a narrow range(s) of composition wavelengths. The structure of a metallic multilayer is remarkably sensitive to the synthesis conditions of the deposition process. Differences that are produced on an atomic scale (as in lattice coherency and composition amplitude) to differences on a microscopic scale (as in grain size, orientation and growth morphology) influence the magnitude of the change in the mechanical behavior. The Supermodulus Effect is known to be linked with the presence of coherently strained layers. This investigation is focused on the microhardness variations of a noble/transition metal system which exhibits the supermodulus effect, specifically Au/Ni multilayers.

An increase of hardness is observed in layered thin films as the layer pair spacing λ decreases. The presence of each layer interface is an obstacle to the passage of dislocations. Thus, the increase in hardness is a result of an increase in the number of interfaces per unit volume. The increase in hardness is found to be inversely proportional to $\lambda^{0.5}$ for simply layered structures. This well-known Hall-Petch relationship is confirmed for both small and large increases of hardness in layered systems. For 0.1 μm Cu/Ni layer pairs the hardness is increased to 300% the rule-of-mixtures value and for 0.2 μm Cu/Fe layer pairs the hardness is increased to 200% the rule-of-mixtures value.^[6] For Cu/Cr laminates, only a 10% increase is found beyond the rule-of-mixtures value.^[7]

The additional presence of lattice coherency, as seen in metallic multilayers with nanometer scaled layer pairs, is found to introduce a local maximum in hardness. The maxima in hardness occurs for layer pairs consisting of 4-6 atomic planes of each metal constituent, wherein the coherency strains have their maximum magnitude. In Au/Ni multilayers, both the in-plane and

normal strain components are maximum for layer pair spacings of $\sim 2\text{nm}$.^[8-9] Microindentation measurements for TiN/VN superlattices oriented along [100] show a maximum hardness which is 275% the rule-of-mixtures value for $\lambda = 5.2\text{nm}$ (i.e. 6 atomic planes of both TiN and VN per layer).^[10] An increase in the Vickers microhardness is similarly measured for TiN/NbN [100] superlattices with a local maximum of a 270% increase for $\lambda = 4.6\text{nm}$.^[11]

For submicron thick films probed with nanometer scaled indentations, a variation in the hardness measured for a single film will occur with different indentation depths.^[12] At some critical depth, the influence of the substrate on the measured film hardness will become pronounced. For the case of films which are soft in comparison to hard substrates, the measured hardness will increase beyond the critical indentation depth. A method of analysis needs to be established in order to determine the hardness of a thin film on a substrate. A technique for determining the critical indentation depth is based on the well-known Meyer relation between the applied load L and the indentation diagonal d .^[13] For bulk materials, a plot of $\log L$ vs $\log d$, generally produces a straight line. For thin film coatings, a deviation from the straight line occurs at the indentation depth where the substrate begins to influence the indentation process.^[14] Hardness values determined below the critical indentation depth D_c are representative of the coating alone whereas values determined above the critical indentation depth represent the film-substrate composite. For multilayer structures, wherein the hardness may vary as a function of layer pair spacing, the critical indentation depth D_c should be ideally determined from Meyer Plots for each sample uniquely. In the analysis presented, Meyer Plots will be constructed using load as a function of the indentation depth D , since the indentation depth is directly proportional to the indentation diagonal.

II. EXPERIMENTS

A. Sample Preparation

The Au/Ni multilayer samples are prepared by planar magnetron sputtering in the dc mode.^[9,15] The deposition is based on the sequential rotation of Si(100) substrates positioned 20 cm above a circular array of individually shielded, sputtering sources. The oxygen-free copper substrate table is maintained near room temperature ($<40\text{ }^{\circ}\text{C}$) during the deposition. The target materials are 0.99995 pure Ni and 0.997 pure Au. A 6.7×10^{-1} Pa working argon gas pressure is used to sputter the target materials whereas the cryogenically pumped system base pressure is 6.7×10^{-6} Pa. A constant deposition flux, between 0.1 and 1.0 nm s^{-1} , is maintained for each multilayer coating. Multilayers with layer pair spacings λ between 0.82 and 9.0 nm (listed in Table I) are prepared in this way where N is the number of layer pairs and t is the film thickness. The nominal composition of each sample, based on calibrated 6 MHz quartz crystal thickness monitors, is $\text{Au}_{0.5}\text{Ni}_{0.5}$. Coatings of Au and Ni, $0.2\text{ }\mu\text{m}$ thick, are prepared for comparison to the Au/Ni multilayer samples.

B. X-Ray Diffraction

The Au/Ni multilayers are characterized with $\text{CuK}\alpha$ x-ray diffraction (XRD).^[8,16] A powder diffractometer equipped with a graphite monochromator is operated in the $\theta/2\theta$ mode. The x-ray diffraction data characteristically show a (111) Bragg reflection with high and low angle satellite reflections (as seen in Fig. 1). The separation measured between the satellite reflections and the Au/Ni(111) Bragg reflection yields an average layer pair spacing for the 9 nm sample. For reference, the (111) interplanar spacings of pure Au and Ni are 0.236 and 0.203 nm , respectively. The full width at half maximum is less than 0.75° for the diffraction peaks of all Au/Ni samples. These Au/Ni multilayers are uniquely textured along the $[111]$ growth direction. The intensities of the satellite reflections about (111) are used to calculate the shape of the composition profile. A

Guinier analysis has been developed to calculate the composition profile from the $\theta/2\theta$ scans.^[17] The analysis yields a square wave approximation of a sinusoidal composition variation for each Au/Ni sample. A dynamical theory of x-ray diffraction is used to fit the $\theta/2\theta$ scans with a strain profile in the composition modulation direction.^[8]

C. Transmission Electron Microscopy

The Au/Ni multilayers are characterized by transmission electron microscopy (TEM) of samples imaged in cross-section. Details of the sample preparation technique for cross-section imaging are presented elsewhere^[15]. Bright field images of samples viewed in cross-section typically show a dense, columnar growth structure with subgrain diameters of 30-60 nm (as seen in Fig. 2). The individual gold (appearing dark) and nickel (light) layers are discrete and continuous across the column boundaries. These Au/Ni multilayers, deposited at room temperature, have a flat surface. (Note that the rms surface roughness as measured using a Nomarski type scanning instrument is found to be less than 0.3nm for all Au/Ni samples.) Selected-area, electron diffraction patterns (SADPs) of the cross-sectioned samples reveal a single to multiple phase transition as the layer pair spacing λ increases^[15]. The reflections of twinned Au(111) and Ni(111) layers are present in the 9nm layer pair SADP (see Fig. 2 insert).

D. Microindentation

Microindentation techniques have been developed to measure hardness from thin films on substrates. The hardness of a film can be determined from indentation load - displacement data.^[18] A NanoIndenter is used to obtain the indentation load - displacement data. Indentation arrays for each sample consist of six indentations at each of six maximum depths. The load is varied from sample to sample in order to achieve the same maximum depths. The indenter is initially loaded at a velocity of 3-6 nm s⁻¹, then held at the peak load until the velocity decreases below 0.1 nm s⁻¹,

and finally unloaded at a constant rate. Loads and indentation depths are measureable above 0.25 μN and to within 0.3nm, respectively. The hardness is equivalent to the peak indentation load divided by the projected contact area of the indenter impression. The contact area is proportional to the square of the indentation depth. The indentation depth is determined by extrapolating the initial 25% of the indentation unloading curve, using a least squares fit of a straight line, to zero load. The method of determining contact area through an effective indentation depth is more accurate than using either the indentation depth at peak load or the final depth. Limitations to the assumptions of linear unloading and the flat punch approximation for the indenter tip can affect the current results by uniformly decreasing the measured hardness values by 10-15%.^[19]

III. MICROHARDNESS RESULTS

The Meyer Plot for the Ni(111) coating, modified to present load as function of indentation depth, clearly shows the transition from indenting only the film to measuring the hardness contribution of the Si(100) substrate (in Fig. 3). Even for indents as shallow as 30nm, the tangent to the load vs depth curve for increasing load shows that the effects of the substrate are just beginning to diminish. The hardness vs indentation depth curves which correspond to the Au and Ni coatings again show the transition of measuring the substrate effect to just the coating hardness as the indentation depth decreases below 4nm (in Fig. 4). The Ni hardness curve shows the transition from the coating (at 7.0 GPa) below a 3-4nm depth to the substrate (at 13.9 GPa) above a 150nm depth. The Au film smears under plastic deformation which masks the full effect of the Si substrate until the depth exceeds the full coating thickness. The Au hardness is measured (at 1.3 GPa) below a 4nm indentation. The continuous change in hardness above indentation depths of 4 nm reflecting the increasing magnitude of the substrate effect show the necessity to use the shallowest indentation depths in order to measure only the coating hardness.

The load vs indentation depth curve of the 9nm Au/Ni multilayer (in Fig. 5) shows the critical indentation depth to be 3 nm. Deviation of the load curve away from the film tangent shows the influence of the substrate as the indentation depth increases. The load vs depth curve is fitted to the average load of six data sets at each indentation depth. A plot of the corresponding hardness values for each 9nm Au/Ni load-indentation depth data set (in Fig. 6) again shows the substrate effect. The hardness continuously increases above an indentation depth of 4nm for the 9nm Au/Ni sample. The hardness of the coating alone just becomes evident below indentation depths of 4nm.

The hardness vs indentation depth curves for all the Au/Ni multilayer samples (in Fig. 6) show the substrate-film average at indentation depths $>100\text{nm}$. The softer coatings (as the 0.82nm sample) produce a lower average than the harder coatings (as the 1.77nm sample). Below the 100nm depth, the hardness continuously changes until the film hardness is measured alone. The critical indentation depth D_c changes for each sample since each film with a different layer pair spacing λ has a unique hardness. Even for the shallowest indentation depth, the effect of the substrate is just becoming minimal. A plot of the hardness variation with layer pair spacing λ is shown for each set of indentation depths (in Fig. 7). The maximum variation in hardness is observed at the shallowest indentation depth (3nm). The rule-of-mixtures value for $\text{Au}_{0.5}\text{-Ni}_{0.5}$ is plotted (as determined from Fig. 3) for comparison to the multilayer results.

The need to use the smallest indentation depth is clear to minimize the substrate effect on measured film hardness. The layer flatness observed in the TEM cross-section micrographs^[9,15] (as Fig. 2) eliminates any concern of surface roughness affecting the hardness variation for decreasing indentation depths. The peak hardness is measured for the $\sim 2\text{nm}$ Au/Ni layer pair spacing. The peak hardness is twice the rule-of-mixtures average (a 100% increase). The 9nm sample increases by only 30%, the least amount for any sample.

IV. DISCUSSION

The hardness values determined for the Au and Ni films, as well as Si, are comparable with results from other microindentation experiments. A nearly identical value is reported for Au (1.0 GPa) using the same indentation instrument^[20], whereas reported values for Ni (4.2 GPa) and Si (9.1 GPa) measured using a 5 gf load in a Vickers indenter^[14] are in correct proportion. The ASTM recommendation^[21] to measure the coating hardness at a indentation depth/film thickness $D/t < 0.1$ is clearly evidenced in this study. Although the critical depth will vary from one Au/Ni layer pair spacing to the next, the affects of the substrate on the hardness measurement are just diminished at $D/t < 0.06-0.08$.

The hardness peak at a layer pair spacing λ of $\sim 2\text{nm}$ is consistent with both the supermodulus peak and magnetic anisotropy energy peak for the Au/Ni system (in Fig. 8). The biaxial modulus is calculated from the spacings of in-plane diffraction peaks.^[9] The total anisotropy energy represents the difference in energy density measured between the parallel and perpendicular states.^[22] (The easy magnetization direction is in-plane.) The origin of all these enhanced physical properties are linked to the underlying microstructure. The superlattice distortions in Au/Ni multilayers have been extensively characterized using XRD and TEM.^[8-9] The dynamical theory of x-ray diffraction is utilized to obtain calculated diffraction curves for each Au/Ni sample by an iterative fitting to the amplitude and angular spacings of the measured (111) Bragg reflection(s) and corresponding satellite peaks. This procedure indicates that the Au and Ni layers are strained along the [111] growth direction. The interface spacings of Au and Ni are equivalent, but relax to unstrained values away from the interfaces. The larger layer pair spacings ($\lambda > 2-3\text{nm}$) have complete relaxation away from the interface into the layer, whereas the shorter layer pairs ($\lambda < 2-3\text{nm}$) do not have complete relaxation. The computed interplanar spacings indicate the nickel layers to be in tension whereas the gold layers are in compression along the modulation direction.

For Au/Ni layer pair spacings $\lambda > 2$ nm, the (111) reflections of the SADP(s) correspond to strained planar spacings. Coincident with the [112] pole projection of the cross-section, diffraction patterns are the (220) reflections. The (220) reflection corresponds to the 'in-plane' spacing which is perpendicular to the (111) spacing of the modulation direction. The (220) is singular for $\lambda < 2$ nm indicating in-plane coherency between the Au and Ni layers. The presence of (220) reflections from Au and Ni are additionally present for $\lambda > 2$ nm. The measured average spacing for the (220) Au and Ni approach unstrained values as the layer pair increases to 4.4 nm, wherein the intermediate spacing corresponding to the interface vanishes.

Intensity traces of digitized high resolution electron microscopy images of samples viewed in cross-section are used to simultaneously generate (111) and (220) Au/Ni spacings. A periodic planar spacing variation along the modulation [111] is revealed through the Au and Ni layers as found by both x-ray diffraction and SADP electron microscopy analysis. Unstrained spacings (111), as measured in the bulk state of nickel and gold, are found away from the Au-Ni interfaces. The average (111) spacings for the Au and Ni layers, in addition to the intermediate spacing of the interface, converge as λ decreases. The average (220) spacings for Au and Ni likewise converge as λ decreases. Both the Au and Ni layers are coherent (in-plane) at $\lambda \sim 2$ nm where the (220) lattice misfit is zero.

The individual layers of Au and Ni do not follow a direct Poisson effect, that is contraction perpendicular to the direction of expansion. The individual layers of Ni expand both in-plane and along the modulation direction, although not necessarily to the same magnitude. The expansion of the Ni lattice may originate to structurally match the Au lattice during the growth process. The mutual solid solubility of Au and Ni does suggest the feasibility of an epitaxial and lattice matched (coherent) growth process. Whereas the local layer distortions do not follow a normal Poisson effect, the averaged planar spacings for the integrated multilayer structure should if the resultant structure behaves as a continuum body. The average Au-Ni planar spacings at each layer pair

spacing λ do follow the Poisson relation. The net in-plane compression accompanied by out-of-plane expansion has been suggested for metallic superlattice systems^[23].

V. SUMMARY

The hardness of Au/Ni(111) multilayers, deposited on Si(100) substrates by magnetron sputtering, is measured using microindentation. The hardness of the coatings is found to be dependent on the layer pair spacing of the multilayer. The indentation depth critically affects the influence of the substrate on the measurement of the coating hardness. Indentation depths below 5-8% of the Au/Ni film thickness are needed to isolate the film contribution. A peak hardness enhancement of 100% is found for $\lambda \sim 2\text{nm}$. The maximum hardness increase of 100% diminishes above and below $\lambda \sim 2\text{nm}$ to a minimum increase of 30%. The dependency of hardness on λ is a behavior that parallels the enhancement of the biaxial modulus found in noble/transition metal multilayer systems. The terminology of a 'Supermodulus Effect' can be extended to the measurement of microhardness as a 'Superhardness Effect'.

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Table 1. Au/Ni Multilayer Sample Dimensions

λ (nm)	0.82	1.24	1.77	2.51	4.41	9.00
N	570	380	193	190	100	25
t (nm)	470	495	390	505	485	230

Figure Captions

1. A $\text{CuK}\alpha$ x-ray diffraction scan of a 9nm Au/Ni multilayer using a powder diffractometer equipped with a graphite monochromator operated in the $\theta/2\theta$ mode. The order of each satellite reflection is indicated above (+) and below (-) the Au/Ni(111) Bragg reflection (0).
2. A transmission electron microscopy bright field image and selected area diffraction pattern of a 25 layer pair 9nm Au/Ni multilayer sample viewed in cross-section reveals a dense, columnar growth structure with a flat surface and both discrete and continuous layering across columnar boundaries. The growth direction is indicated with an arrow.
3. A microindentation load vs indentation depth plot of a 0.2 μm thick Ni coated Si(100) substrate.
4. The hardness vs indentation depth plots of Au(111) and Ni(111) coated Si substrates show the transition from measuring the hardness of the coating to sensing the effect of the substrate as indentation depth increases.
5. A microindentation load vs indentation depth plot of a 9nm Au/Ni multilayer coated Si(100) substrate.
6. The hardness vs indentation depth plots of Au/Ni(111) multilayer coated Si substrates show the transition from measuring the hardness of the coating to sensing the effect of the substrate as indentation depth increases.
7. A local maximum is measured for the hardness vs layer pair spacing plots of Au/Ni(111) multilayer coated Si substrates.
8. A local maximum is measured for the magnetic anisotropy energy^[22] and calculated for the biaxial modulus^[9] variation with layer pair spacing of Au/Ni multilayer samples.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

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