Department of Physics
College of Arts & Sciences
Faculty of Science

THE UNIVERSITY OF
ARIZONA®
TUCSON ARIZONA

1118 E. 4th Street
Tucson, Arizona 85721
(602) 621-6820

December 1, 1994

Dr. Richard Brandt
Code ONR 312
Physics Division
Office of Naval Research
800 North Quincy
Arlington, Virginia 22217

RE: ONR Contract N00014-88-K-0298
ONR Grant N00014-91-J-1104

Dear Dick:

Enclosed are two re-revised copies of the final report on our elastic properties contract. The report I mailed to you with a cover letter dated November 21st did not reference the ONR grant. I apologize for this oversight and any inconvenience it may cause.

Sincerely,

Charles M. Falco
Professor: Physics; Optical Sciences

CMF:mb

Enclosure: Two copies of Final Report on
ONR Contract N00014-88-K-0298,
ONR Grant N00014-91-J-1104

cc: Max Irving (with one copy of the report)
Defense Technical Information Center (with one copy of the report)

Final Report
(revised 11/21/94; 11/30/94)

ELASTIC PROPERTIES OF METALLIC SUPERLATTICES

ONR Contract N00014-88-K-0298
and ONR Grant N00014-91-J-1104

Charles M. Falco, PI
George I. Stegeman, Co-PI
Arizona Research Laboratories
University of Arizona
Tucson, Arizona 85721
(602) 621-6771
(602) 621-4356 FAX

I. Introduction

This Final Report describes some of the significant results from our research program on the elastic properties of metallic multilayers and superlattices. This work resulted in 20 papers (listed at the end of this report) submitted to various refereed journals, as well as 10 invited talks at international conferences.

The elastic properties of composition-modulated metallic superlattice films have received considerable attention over the past fifteen years following the initial reports of anomalous enhancements of some elastic moduli as measured by the bulge tester method.[1,2] For example, it was reported that the Ag/Pd system exhibited an increase of the biaxial modulus of up to 500%.[1] However, more recent measurements[3,4] failed to reproduce such large enhancements of elastic moduli in the systems for which the elastic anomaly was originally measured.[1,2] The elastic anomalies observed in subsequent experiments[5–8] were considerably smaller, although they showed a functional dependence on Λ, with either stiffening or softening taking place in different material systems for Λ in the range of ≈25–40 Å. In apparent contrast, some Brillouin light scattering (BLS) measurements have shown a softening of the shear elastic constant c_{44} in some bcc/fcc systems,[5,6,8] although a stiffening was found in Au/Cr.[9] Because of these apparent contradictions, coupled with the importance of this problem, we initiated a program with ONR funding to investigate these effects. In this report, we review some of our significant results obtained with ONR funding, on the structural and elastic properties observed metallic superlattice films.

II. Sample Preparation

We used magnetically-enhanced dc-triode sputtering to prepare several series of Ag/Pd and Cu/Pd superlattice films with Λ ranging from 5 Å to 130 Å. The total film thicknesses were between 4100 Å and 4500 Å. The base pressure was typically 2.0×10^{-7} torr, and the Ar sputtering pressure was 6–7 mtorr. The sputtering rates used were (a) 20.9 Å/sec for Ag and 18.0 Å/sec for Pd for the Ag/Pd, and (b) 7.1 Å/sec for Cu and 9.0 Å/sec for Pd for the Cu/Pd, respectively. The films were deposited on single crystal 90° (Ag/Pd) and 0° (Cu/Pd) sapphire substrates at ambient temperature. The compositions of the first series of Ag/Pd films and of the Cu/Pd films were 51.6 at. % Pd and 49 at. % Pd, respectively. We also prepared two co-deposited samples to study uniform Ag-Pd alloy films. For these samples the sputtering rates were 6.8 Å/sec for Ag and 6.7 Å/sec for Pd, respectively, for a composition of 53.8 at. % Pd. The total thicknesses of the as-deposited alloy films were about 3300 Å.

A-1

In addition to the sputtered samples, we prepared a number of metallic superlattices by Molecular Beam Epitaxy (MBE).

III. Structural Properties

We characterized the structure of our films using θ-2θ x-ray diffraction with CuKα radiation. Well-defined superlattice peaks were clearly observed from films with $\Lambda > 25$ Å. For the films with $\Lambda \leq 25$ Å, however, diffraction from the fundamental [hkl] crystal orientations allowed for fcc materials was observed without showing the x-ray satellite peaks.

Using Scherrer's equation, we determined the structural coherence length ξ by deconvolving the instrumental linewidth from the full width at half maximum (FWHM) of the central [111] Bragg peak. Plotting the normalized structural coherence length ξ/Λ against $1/\Lambda$ allowed us to demonstrate that two regimes are apparent, with a change in the behavior of ξ/Λ at critical modulation wavelength $\Lambda_k \approx 20$ Å. The change in slope and the rapid increase of ξ/Λ for $\Lambda < \Lambda_k$ were reproducible in films that were prepared months apart.

The measured lattice spacing d in the growth direction showed only a small change with Λ. The homogeneous strain changed by only 0.6% in both series of samples with $\Lambda \leq 20$ Å, while it remained constant to within 0.2% for $\Lambda > 20$ Å. In addition, from the measured lattice spacings of the films with $\Lambda \leq 25$ Å, we determined the average cubic lattice constant a by linearly fitting the lattice spacing d[hkl] to the value $(h^2+k^2+l^2)^{-1/2}$. As Λ is decreased, the fitted lattice parameter values a approach the value $a_{th} = 3.987$ Å ($a_{th} = 3.983$ Å for the second series of films) calculated using Vegard's law for a homogeneous Ag-Pd alloy film. The total deviation of the fitted lattice parameter values from a_{th} is between +0.4% and –0.2%.

We chose a Ag/Pd superlattice film with $\Lambda = 60$ Å and a co-deposited Ag-Pd alloy film to study the effect of thermal annealing on their structural and elastic properties. The films were held at 375 °C for 65 min. and then were cooled to room temperature. The chemical modulation of the as-grown superlattice film disappeared during the annealing, as evidenced by the disappearance of satellite lines. This indicates that the sample underwent a complete intermixing of Ag and Pd. The homogeneous strain changed from +0.22% (tensile) to –0.74% (compressive). The structural coherence length in the growth direction increased by 54% from 289 Å to 445 Å. Also, considerable [200], [220], and [311] film textures appeared. On the other hand, the x-ray diffraction spectrum of the co-deposited alloy film during the annealing is improved in that the linewidths narrowed significantly and peak intensities increased approximately threefold. As will be described in the following section, the shear elastic constant c_{55} of the annealed films enhanced significantly.

In a detailed x-ray diffraction study of our Cu/Pd superlattices we observed that the films had strong [111] texture along the film normal. The presence of satellite peaks confirmed good structural and chemical modulation of the superlattice films down to $\Lambda = 10.5$ Å with an abrupt change of its composition at the interfaces.

Unlike the Ag/Pd films, we observed strong Λ dependence of the measured average lattice spacing d in the [111] direction. By plotting the measured homogeneous strain $(d-d_0)/d_0$ normal to the film plane as a function of Λ we were able to show that the average lattice spacing d exhibited a slight (~0.4%) expansion for Λ down to ≈38 Å, and then a rapid contraction by 0.7% as Λ is further decreased.

We observed that the normalized structural coherence length ξ/Λ for the Cu/Pd samples was linearly dependent on $1/\Lambda$ without a kink as was found for Ag/Pd. The loss of coherency with Λ in a multilayer can result from interfacial disorder induced by the lattice mismatch, and that this effect is common for immiscible crystalline-crystalline superlattice films with sharp interfaces. Our results show that despite their solubility, the Cu/Pd superlattice films consist of sharp but rough interfaces whose roughness is inversely proportional to the modulation wavelength.

IV. Elastic Properties

The elastic constants of metallic films can be determined from Brillouin light scattering (BLS) measurements of the Rayleigh and Sezawa film guided acoustic-mode velocity dispersion. We developed techniques to obtain the individual elastic constants by a least-squares fit of the dispersion of the calculated film-guided mode velocities to that of the measured velocities. For sputtered films which have hexagonal symmetry, the velocities of these modes are determined by four of the five independent elastic constants: c_{11}, c_{13}, c_{33}, and $c_{55}=c_{44}$. The Rayleigh sound velocity v_R is primarily determined by c_{55}.

In Brillouin-light-scattering studies of a series of Ag/Pd superlattice films we were the first to observe scattering from longitudinal guided modes (LGMs) in a metallic thin film of any kind. LGMs are film-guided acoustic modes which have displacements primarily along the propagation direction in the film plane, and velocities that are strongly dependent on the longitudinal elastic constant c_{11}. From the measured velocity of the first-order LGM, we obtained the first accurate determination of c_{11} for metallic thin films.

With our BLS studies we showed that c_{55} increases monotonically as Λ decreases below 60 Å to 5 Å. The total change in c_{55} is the largest change observed to date for any metallic superlattice system. The values of c_{11} also increase monotonically as Λ decreases. The total increase in c_{11} is 14%. It is possible that this monotonic behavior of c_{11} and c_{55} is due to the presence of stiff interfaces between the Ag and Pd layers, since the interface contribution to the elastic constants becomes increasingly more important as Λ is decreased. Ag/Pd is the first metallic superlattice system for which both the longitudinal c_{11} and shear c_{55} elastic constants are found to have the same qualitative Λ dependence.

As mentioned earlier, in a set of *in situ* BLS measurements taken during annealing, we observed a dramatic enhancement of Rayleigh wave velocity v_R in the Ag/Pd superlattice film. The shear elastic constant c_{55} was increased by a 50% from 29 GPa to 44 GPa, while the compressional elastic constants c_{11} and c_{33} were enhanced by about 10%. Likewise, the v_R of the annealed co-deposited alloy film changed to 1850 m/sec from 1660 m/sec. The increased value was as large as those of Ag/Pd multilayer films with small $\Lambda \leq 10$ Å.

V. Discussion

Our observations were the first to suggest that Ag/Pd superlattices undergo a structural transformation as Λ is decreased below $\Lambda_k \approx 20$ Å. From the loss of x-ray satellite lines associated with film textures in all allowed reflections for fcc crystals and a sudden increase of structural coherence length for $\Lambda \leq \Lambda_k$, at Λ_k the film is no longer a one-dimensional superlattice structure but rather is a solid solution alloy throughout the whole film thickness. It is possible that the small change of the lattice spacing d within 0.2% for $\Lambda > 20$ Å results from interdiffusion of Ag and Pd at the interfaces such that the strain energy at the interfaces is completely released.

A slight contraction for $\Lambda \le \Lambda_k$ was apparently caused by alloying to a Ag-Pd solid solution, as observed in the Ag/Pd superlattice film during annealing.

For a set of particular growth conditions for Ag and Pd, Λ_k defines the value at which the films transform from multilayered structures to homogeneous alloys. Thus, we were able to infer that the thickness of intermixing is $t_{int} \approx 10$ Å. Independently, we obtained the same value of $t_{int} = 11$ Å from a fit to the measured dependence of c_{55} and c_{11} on $1/\Lambda$. For $\Lambda > \Lambda_k$, films develop into superlattice structures with three layers within a modulation wavelength. That is, a Ag and a Pd bulk layer and a 10 Å thick intermixed Ag-Pd alloy layer at each interface.

For the films with $\Lambda \le 25$ Å, the observed Rayleigh sound velocity v_R increased by 10% and showed a very good correlation with the structural coherence length ξ in the [111] direction. A 12% enhancement of v_R in the co-deposited film during annealing is related to the increase of 260% increase of ξ. This is consistent with large increase of both c_{55} and ξ[111] observed for the annealed Ag/Pd superlattice film. This indicates that diffusion-induced crystallization of the Ag-Pd alloy is correlated to the large increase of Rayleigh sound velocity v_R for $\Lambda \le \Lambda_k$.

Localized strain at interfaces being responsible for a change of acoustic wave velocity is, we believe, not unique to particular metallic systems. As shown below, there is strong evidence that interfacial strain in the Cu/Pd superlattice films is ultimately responsible for the softening of the shear elastic constant c_{55} with Λ.

The relative change in the average lattice spacing d to the unstrained d_0 can be written as $(\Delta d/d) = 2\delta\cdot(1/\Lambda)$, where $\Delta d = d - d_0$, $\delta = d_{int} - (d_{Cu} + d_{Pd})/2$ and d_{int} is the strained interfacial lattice spacing. We found that Δd exhibits an excellent linear relationship with $1/\Lambda$. The interfacial strains extracted from straight line fits to our data are –2.2% for $\Lambda < 38$ Å and +3.6% for $\Lambda > 38$ Å. This indicates that the interfaces are under compressive stress (negative slope) for $\Lambda < \Lambda_c$ and tensile stress (positive slope) for $\Lambda > \Lambda_c$. At the point Λ_c where the interfacial strain turns from tensile to compressive the shear elastic constant c_{55} has its minimum value. Although the softening of c_{55} with Λ that we measured is related to the change in the homogeneous elastic strain in the growth direction, the total change in strain throughout the whole sample range is only a 0.7%. Such small total strain change with Λ is the result of a large interfacial strain associated with an interface density that is inversely proportional to Λ. Thus, we conclude that the softening of c_{55} originates from the interfacial strain and interface density.

VI. Summary

With our ONR funding we were able to conduct a series of high sensitivity Brillouin light scattering (BLS) studies on carefully-prepared, extensively-characterized metallic multilayer samples. Our significant results include the observations of a 50% stiffening of c_{55} and a 14% stiffening of c_{11} in the Ag/Pd system, and a 25% softening of c_{55} in the Cu/Pd system as Λ was decreased. Our detailed structural studies on these materials allowed us to conclude that for the Ag/Pd films the presence of an intermixed, extended interface layers (rather than a "superlattice" or "supermodulus" effect) is responsible for the large enhancement of c_{55}, disappearance of the multilayered structure, and increase in the degree of structural order. However, for the Cu/Pd films interfacial strain is responsible for the softening of c_{55} with Λ. We also extended the BLS technique to make the first observations of Longitudinal Guided Modes in metallic thin films of any type.

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