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THE CORRELATION OF STRESS-STATE AND NANO-MECHANICAL PROPERTIES IN AU

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ABSTRACT

A dependence of elastic response on the stress-state of a thin film has been demonstrated using the interfacial force microscope (IFM). Indentation response was measured as a function of the applied biaxial stress-state for 100 nm thick Au films. An increase in measured elastic modulus with applied compressive stress, and a decrease with applied tensile stress was observed. Measurements of elastic modulus before and after applying stress were identical indicating that the observed change in response is not due to a permanent change in film properties.

INTRODUCTION

The determination of the mechanical properties of nanostructured materials is critical to the continuing development of thin film technology. In particular the correlations between the mechanical response, residual stress state and deposition conditions have been documented for several systems but are not well understood [1-4]. Several of these reports have shown evidence of properties unique to nanocrystalline materials, when compared with conventional polycrystalline materials. These unique nano-mechanical properties have generally been attributed to the material's high defect densities and or changes in the mechanisms accommodating deformation [1,3,4].

This investigation of mechanical response as a function of stress state was prompted by a previous IFM survey of the mechanical response of 200 nm thick Au films deposited on various substrates using different deposition conditions [3]. For these samples, measurements of elastic moduli were consistent from point to point and sample to sample for samples made with similar deposition conditions. However large sample to sample variations were observed as a function of film adhesion-layer combinations and substrate temperature during deposition. These variations in mechanical response were found to correlate with the samples' residual stress state and not with morphology or substrate adhesion. In order to better establish the details of this relationship, a concentric ring bending device was built to investigate the dependence of IFM nanoindentation measurements on applied tensile and compressive stresses.

A dependence of nanoindentation response on stress state has been discussed in several reports [1,5,6]. Most of these authors document changes in hardness with stress state. In the cases where a dependence of elastic modulus upon stress state was observed it was generally explained as a measurement artifact. Tsui, Oliver and Pharr recently analyzed the influence of stress applied to a bulk aluminum alloy on the measurement of hardness and elastic modulus [5,6]. Their nanoindentation measurements showed a 20% variation in these values with applied stresses in the range of -250 to 250 MPa [5]. A subsequent analysis of a finite-element model of the indentation suggested this was an 'artificial' dependence, due to an improper estimation of the probe-surface contact area as a

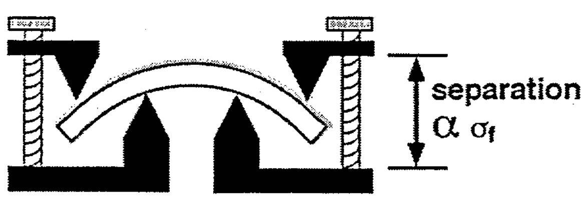
result of the pile-up which occurs during indentation [6]. To avoid a dependence on pile-up formation and the generation of defects during the measurement, the elastic response was measured before the onset of plasticity for the work presented in this paper.

THE EXPERIMENT

Measurements of indentation response as a function of applied stress were performed on two Au thin film samples. 100 nm thick Au films (on 10 nm of Cr or Ti) were prepared by e-beam evaporation (1 nm/sec) onto 25 C Si substrates. The Si substrates were HF dipped before being placed into the evaporation chamber (10^{-6} torr) and then Argon sputtered for 30 sec before deposition(s). Previous analysis of these films suggests a columnar grain structure, a predominately <111> texture, and an average grain diameter of 80 nm. The residual and applied stress-states of these films were determined from interferometric measurements of wafer curvature. The residual stress of the Au/Cr/Si and Au/Ti/Si samples was measured to be 100±25 MPa tensile and 50±25 MPa respectively. Measurements of wafer curvature before and after applying stress indicate that the residual stress remained constant throughout the measurements.

The IFM is uniquely suited for nanoindentation since it combines the advantages of a stable feedback controlled load sensor [3] with the small mechanical loop and imaging capability of a scanned probe microscope. The IFM force-distance relationship was quantified by measuring the machine compliance (>3000 N/m) and the sensitivity of the IFM load sensor (100 μN/V) using a laboratory microbeam balance [7]. It was not necessary to correct any of the load curves measured in this study for machine compliance or drift. Drift along the load axis was consistently less than 0.1 nm/s and load sensor drift of less than 15 nN/s was typical. Load displacement curves were acquired under displacement control at 0.1-1 Hz, therefore these drift values cause less than 1% error of the load and displacement axes.

A concentric ring bending device has been built with which it was possible to mechanically and controllably vary the stress state of a film from 50 MPa compressive to -50 MPa tensile with a ±10 MPa uncertainty, as shown in Figure 1. Fracture of the Si substrate prohibits the application of higher stresses. The stress applied to the thin film is calculated from a measurement of the applied curvature as given by Equation 1. In this way the IFM measurements of elastic modulus can be correlated directly with the applied stress, while the morphology of the film and adhesion to the substrate remain constant.



$$\sigma_f = \frac{-t_s \cdot E_f}{2 \cdot R_s \cdot (1-\nu_f)} \qquad (1)$$

Figure 1. Concentric ring bending device

The Au thin film samples were piranha cleaned, placed in a 1 milli-molar ethanol-alkene-thiol solution for 12 hours, and ethanol rinsed before being placed in the concentric ring bending device for measurement. The self-assembling alkene-thiol passivates the chemical and adhesive interactions between the indenter and Au [3]. Passivation of these interactions is required for forming an elastic contact between the indenter and sample. Using the IFM, parabolic diamond indenters (100 nm and 250 nm radius) were indented into the samples while clamped in the bending device. Seven load displacement curves were recorded, at different places on the sample, for each applied stress condition to determine the average response of the sample. In this manner, the elastic loading response was measured before, after and while applying compressive and tensile stress.

THE ANALYSIS

The dependence of elastic response on stress state was quantified by carefully controlling the IFM measurement and the indenter-Au interaction. For the work presented in this paper a Hertzian model [8] is used to analyze the initial elastic response of a film to loading, thereby determining the properties of the sample without first plastically deforming it. Application of the Hertzian model requires a quantitative measurement of the force-distance relationship, a linear-elastic interaction (no adhesion) between the indenter and surface, and a known indenter geometry. The elasticity of the indenter-Au contact was confirmed by the lack of hysterisis in the load-displacement curves (measurements to peak loads of less than 5 μN) and by comparing the images acquired before and after indentation. A study of surface response with and without the monolayer indicates that the presence of a passivating monolayer causes the load response to deviate slightly from Hertzian for indentation depths of less than 2nm. Indenter geometry was controlled using a FIB shaping process described elsewhere [9], and characterized using a JOEL6400FE field emission scanning electron microscope and probe characterizers available from NT-MDT [10]. A parabolic geometry was chosen as it is ideally suited for establishing a predictable elastic contact with the sample.

By carefully controlling the experiment, the relationship between load and deformation closely follows the classical Hertzian model for a rigid, non-interacting parabolic punch deforming an elastic half space, and is given by:

$$\mathbf{F = E^* \ (R^{1/2}) \ d^{3/2}} \qquad (2)$$

where E^* the measured modulus is given by: $1/E^* = (1\text{-}v_i)/E_i + 1\text{-}v_s)/E_s$

and E_i = elastic modulus of indenter = 1100 GPa

E_s = elastic modulus of the sample

d = indentation depth

R = indenter radius

Equation 2 relates the initial loading response of a surface to its elastic modulus. The indentation depth, d, is controlled using the z-piezo of the IFM, and the radius of the indenter, R, is determined from the SEM or probe characterizer images. Equation 2 was fit to the initial loading response and the measured elastic modulus was determined from this fit.

RESULTS

To illustrate the dependence of measured elastic response upon applied stress, the loading portions of three load-displacement curves have been plotted on the same axes as Figure 2. These measurements were acquired by indenting a R = 100 nm diamond indenter into a 100 nm thick Au/Cr/Si sample clamped in the concentric ring bending device. Figure 2 shows the force acting on the diamond plotted as a function of z-piezo position for three different applied stress conditions. The loading response of the thin film in the unstressed case is shown as by the dotted line. The loading response while compressive stress was applied is shown as the dashed line and the response while tensile stress was applied is shown as the broken line. The Hertzian fits used to determine the elastic moduli from these measurements are shown as the solid lines. The dependence of the film's initial loading response upon applied stress can be observed by comparing these curves. When a compressive stress is applied to the film the load increases more rapidly with displacement (dashed line) than in the unstressed (dotted) case. With a tensile stress applied, the load increases less rapidly (broken) than in the unstressed (dotted) case. This difference in the initial loading response of the thin film reflects a change in the film's measured elastic response. This change was quantified by using the Hertzian fit (solid lines) to obtain a measured modulus from each load-displacement curve.

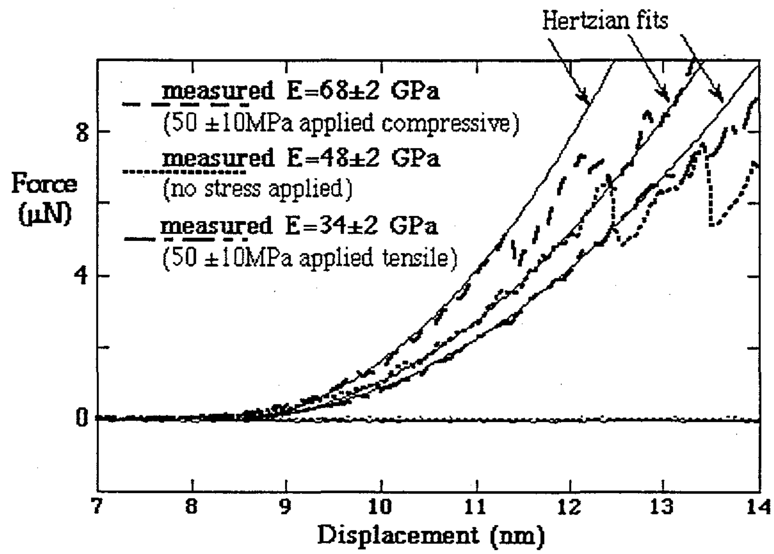


Figure 2. Load-displacement curves for three applied stress conditions

The dependence of measured elastic modulus on applied stress is summarized in Figure 3. Each data point represents an average of the moduli obtained from seven load-displacement curves for a particular applied stress condition. The y-axis error bars are the standard deviation of the moduli measured for each condition. The x-axis error bars are the uncertainty of the applied stress values. Every data point is labeled with a number which reflects its position in each measurement sequence. For example, data point 1 represents the average elastic response measured for the first applied stress condition: unstressed. Data point 2 reflects the second set of load curves of the sequence, made on the same Au/Cr/Si sample with 5 ±10 MPa stress applied. The solid line represents the entire sequence of measurements (1-8) performed on this sample. The elastic response measured with the sample unstressed, mounted on the sample stage, is shown by points 1,5 and 8. Within experimental uncertainties, the same response is measured when less than 10 MPa of stress is applied to the film with the sample mounted in the bending device, as shown by points 2, 4 and 7. The response of the film measured when compressive stress was applied was consistently above, and when tensile stress was applied, consistently below the average unstressed response as shown by points 3 and 6. This measurement sequence (1-8 in Figure 3) illustrates the observed dependence of the elastic loading response upon applied stress. Two additional experiments were performed in an effort to confirm this dependence. The dashed line represents data from a similar measurement sequence (points <u>1-3</u> in Figure 3) performed on the same Au/Cr/Si sample. The dotted line represents data from another measurement sequence (points *1-3* in Figure 3) performed on an Au/Ti/Si sample.

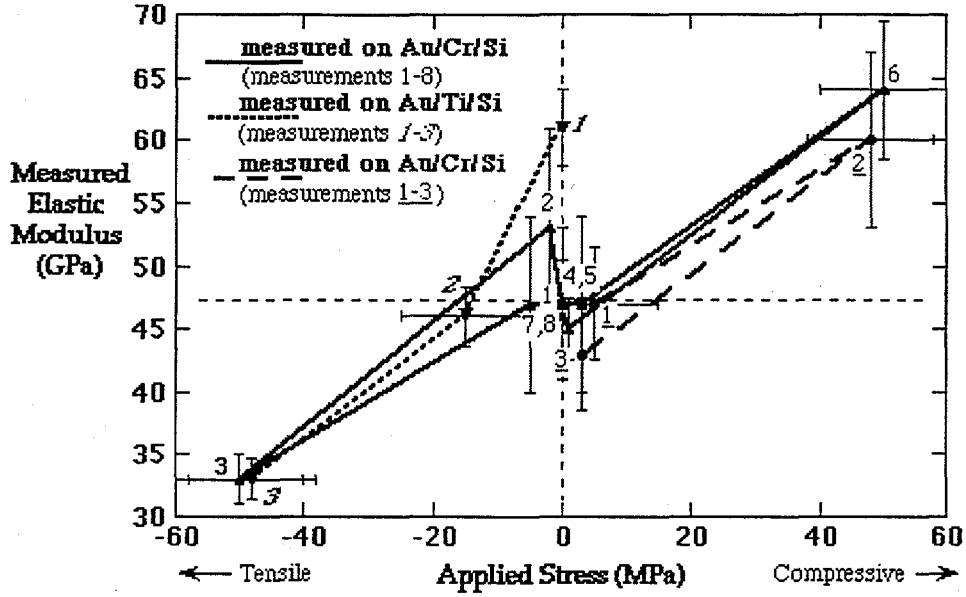


Figure 3. Dependence of elastic loading response upon applied stress (numbers reflect the measurement sequence)

CONCLUSIONS

A dependence of the measured thin film elastic response on stress has been demonstrated using the IFM and a concentric ring bending device. The measured elastic modulus was shown to increase to 65±6 MPa with applied compressive stress (50±10 MPa) and decrease to 32±5 MPa with applied tensile stress (-50±10 MPa). The response of the unstressed film was 47±6 MPa throughout the measurement sequence demonstrating that the change in measured elastic modulus with applied stress is a reversible effect.

The observed dependence of elastic loading response on stress state is either due to a change in the thin film's mechanical response or a repeatable measurement error. Nanoindentation measurements are sensitive to changes in instrument performance and indenter-surface contact area. A dependence due to a change in the compliance of the concentric ring bending device is unlikely since a decrease in elastic modulus measured while the stiffness of the concentric ring bending device increases with applied tensile stress. Variation of the indenter-surface contact area can reasonably account for the 5% variation of measured modulus from load curve to load curve. However, factor of four changes in contact area would be necessary to explain the 30% change with applied stress observed in these measurements. Changes in the indenter geometry, load sensor performance, or z-piezo sensitivity of the IFM would be manifest as changes in response independent of the applied stress condition. Substrate and residual stress effects should have remained constant during these measurements. Changes in instrument performance, or contact area do not appear to account for the observed dependence upon applied stress.

The dependence of thin film elastic response upon stress state reported here is not consistent with measurements performed by Tusi et al. on conventional polycrystalline materials [5]. Instead, the results presented here suggest that the elastic response of thin films, due perhaps to their small grain size or high grain boundary and defect densities, may be dependent upon their stress state. This observed dependence is consistent with that reported in molecular-dynamics simulations performed by Shenderova et al. [11]. In future work the mechanism(s) which explain this dependence of measured elastic modulus upon stress state will be addressed in more detail. These experimental results suggest that the

IFM used in a nanoindenter mode has the potential for being able to measure stress state on a very local level.

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